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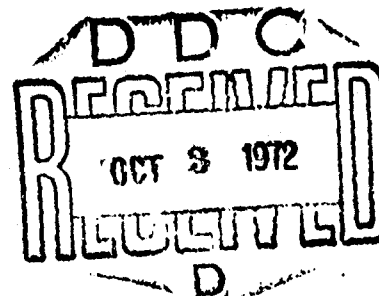
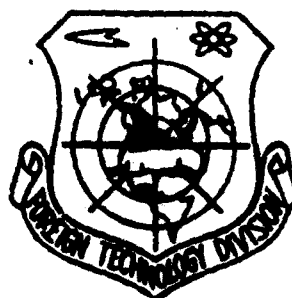
FOREIGN TECHNOLOGY DIVISION



COMBUSTIBLE GASES AND THEIR PROPERTIES

by

V. V. Murzakov



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U. S. BOARD ON GEOGRAPHIC NAMES TRANSLITERATION SYSTEM

Block	Italic	Transliteration	Block	Italic	Transliteration
А а	<i>А а</i>	A, a	Р р	<i>Р р</i>	R, r
Б б	<i>Б б</i>	B, b	С с	<i>С с</i>	S, s
В в	<i>В в</i>	V, v	Т т	<i>Т т</i>	T, t
Г г	<i>Г г</i>	G, g	У у	<i>У у</i>	U, u
Д д	<i>Д д</i>	D, d	Ф ф	<i>Ф ф</i>	F, f
Е е	<i>Е е</i>	Ye, ye; E, e*	Х х	<i>Х х</i>	Kh, kh
Ж ж	<i>Ж ж</i>	Zh, zh	Ц ц	<i>Ц ц</i>	Ts, ts
З з	<i>З з</i>	Z, z	Ч ч	<i>Ч ч</i>	Ch, ch
И и	<i>И и</i>	I, i	Ш ш	<i>Ш ш</i>	Sh, sh
Й й	<i>Й й</i>	Y, y	Щ щ	<i>Щ щ</i>	Shch, shch
К к	<i>К к</i>	K, k	Ъ ъ	<i>Ъ ъ</i>	"
Л л	<i>Л л</i>	L, l	Ы ы	<i>Ы ы</i>	Y, y
М м	<i>М м</i>	M, m	Ь ь	<i>Ь ь</i>	'
Н н	<i>Н н</i>	N, n	Э э	<i>Э э</i>	E, e
О о	<i>О о</i>	O, o	Ю ю	<i>Ю ю</i>	Yu, yu
П п	<i>П п</i>	P, p	Я я	<i>Я я</i>	Ya, ya

* ye initially, after vowels, and after ъ, ь; e elsewhere.
 When written as ѐ in Russian, transliterate as yě or ě.
 The use of diacritical marks is preferred, but such marks
 may be omitted when expediency dictates.

Combustible gases and their properties.
Murzakov, V. V. Leningrad, Nedra, 1970.
(Library for the Gas Industry Foreman). 128 pp.

This pamphlet examines the following: the basic types of gas fuel and methods of obtaining it; physical and chemical properties both of fuel gases and of the products of their combustion, along with the basic questions connected with the combustion process, such as the mechanism of the interaction of the fuel gas with air, ignition of the gas/air mixture, and carburation in laminar and turbulent flames during combustion of both pure gas and a gas/air mixture. Attention is also given to questions of the movement of gas over pipes and other channels with determination of the pressure losses which occur.

The pamphlet is intended for the layman. Its material is outlined in a form sufficiently simple to prevent inadequate training of the reader in the fields of physics, chemistry, and mathematics from presenting an obstacle to a clear understanding of it.

One table, 52 illustrations, and a bibliography of 11 entries.

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FROM THE PUBLISHER

With every passing year the fraction of gas utilized in the fuel equation of the Soviet Union increases; ever more industrial, public-utility, and residential consumers convert to gas. The number of people occupied with servicing equipment using gas is growing constantly.

The training of skilled workers in the assembly, production, adjustment, operation, and repair of gas facilities is the most important condition for effective and safe utilization of gas fuel. At the same time the industrial technical literature available for education, self-study, and skill improvement for the cadres of skilled workers is inadequate. In this connection the Leningrad Branch of the publishing house "Nezra" undertook in 1963 to issue the series "Library for the Gas Industry Foreman," intended primarily for operators, firemen, machinist, fitters, and foremen in the gas industry. The books of the "Library" will also meet the needs of all engineering and technical personnel of the gas industry and establishments.

The "Library" consists of a series of books concerned with the supply and utilization of gas. In particular the following questions are examined: fuel gases and their properties, principles of gas engineering, municipal systems for gas distribution, gas regulation points and installations, control and measuring

instruments in the gas industry, the use of compressed gases, the structure and operation of gas burners of various types, supply of gas to living quarters, municipal buildings, and industrial establishments, burning of gas in boilers and industrial furnaces, automatic regulation and safety of boilers, and the use of gas in agriculture, transportation, etc.

Considering that not a single one of the 33 books published in the period 1963-1969 is available in stock, and that the requirement for them has not been satisfied, in 1965 the publisher began reissuing individual volumes. At the same time the publication of new books is being continued.

We request that remarks, opinions, and suggestions on either the entire "Library" or on individual issues be directed to the following address: Leningrad, S-171, Farforovskaya Street, 12, Leningrad Branch of the Publishing House "Nedra."

Information concerning books of the "Library" in preparation for publication can be obtained from the same address.

To purchase the books of the "Library" it is necessary that before the volumes appear the order be directed to the stores of local book dealers or to the "Nedra" store Lenknigi at the address: Leningrad, V-178, Sredniy Prospekt, d. 45. Upon publication the books will be forwarded by C.O.D. mail.

INTRODUCTION

Fuel gases of natural origin have been known to humanity since deepest antiquity; however, for a long time they were used mainly for ritual purposes. Thus, in many countries of the Near East where natural sources of fuel gases have been known since olden times, the religion of fire-worship was widespread in its time. Natural gases had no substantial national economic significance until the first decades of this century.

In this respect they were preceded by artificial gases, mainly coke gas. Obtained in large quantities during the coking of coal, this gas found use as a fuel as early as the beginning of the Nineteenth Century, while in the second half of that century it found wide use in street and home lighting in large cities. At this time it was even called illuminating gas.

In connection with the broad development of electrical illumination. at the beginning of this century artificial gases came to be applied mainly for heating in residences and as high-quality industrial fuel which possesses many advantages over other types of fuel. No natural gas was utilized in pre-Revolutionary Russia. Even casing-head gas, obtained as a by-product of petroleum extraction, was either burned off or simply allowed to escape into the atmosphere. The first steps in collecting and making rational

use of casing-head gas and also in extracting gas from pure gas deposits were made only in the Soviet period, in the years of the first five-year plans.

The development of the natural gas industry in the Soviet Union began during the Great Patriotic War. The major fuel resource of that time - the Donbass - was temporarily occupied by the enemy and the transportation of fuel was interfered with. Many regions of our country began to convert to local fuels. One of these was the Kuybyshev industrial region, which obtained natural gas from the Buguruslan deposits in 1943, when the first huge Buguruslan-Kuybyshev gas pipeline, about 160 km long, was completed and became operational. In this same year the Yelshanka-Saratov pipeline was completely constructed in twenty days and the large establishments and power stations at Saratov were converted to natural gas. In the middle of 1946 the first long pipeline in our country, the Saratov-Moscow line 850 km long, was completed and became operational; it was based on the Yelshanka and other Saratov deposits of gas.

However, no very great hopes were rested on natural gas at that time, since it was considered that the gas reserves in our country were not great and would be adequate only for a few decades. Reality refuted these pessimistic forecasts. One after another the richest deposits of natural gas were discovered. In the 1948-1956 period several vast deposits were discovered in Stavropol' and in the Krasnodar region, and in 1956 the unique Shebelinsk deposit in the Ukraine was opened; at present this yields about 20% of the total extraction of gas in the nation. Later even larger deposits were found in Central Asia, in the northern portion of the Tyumen' Oblast, and in the Yakutsk ASSR. At present there are about 550 known gas deposits on the territory of our country, with the predicted reserves comprising 60,000 billion m³.

In parallel to the discovery of gas deposits there was a vigorous growth in gas extraction (Fig. 1). The figures shown on the graph include production of artificial gas from coal and shale on special gasworks. However, the total volume of artificial production is comparatively small: in 1955 a total of 1.3 billion m^3 ; by 1960 it had risen to 1.9 billion m^3 , and subsequently it even began to decline. By 1970 its production had stabilized at the 2 billion m^3 /year level. The last 7-8 years have seen a particularly sharp growth in the volume of natural gas extraction. According to statistical data, the fraction of natural gas (together with by-product casing-head gas) in the fuel balance of our country grew from 9.7 to 17.2% from 1961 through 1967. In a number of economic regions gas has become the basic type of fuel. Thus, at the beginning of 1968 the fraction of gas in the fuel balance for the Central Asian region exceeded 35%, for the Transcaucasus and the Center region it comprised about 40%, while in the Northern Kavkaz it was almost 50%.

The following data indicate the sharp increase in the use of gas by the major categories of consumers in this period (figures given in billion m^3):

	1961	1967
Public and municipal consumers....	6.5	20.4
Industry (excluding electric power).....	34.2	91.1
including:		
chemical industry.....	2.2	8.9
ferrous and nonferrous metallurgy.....	7.3	26.3
Electric power stations.....	16.1	40.9
Other consumers.....	2.2	5.0
Total:	59.0	157.4

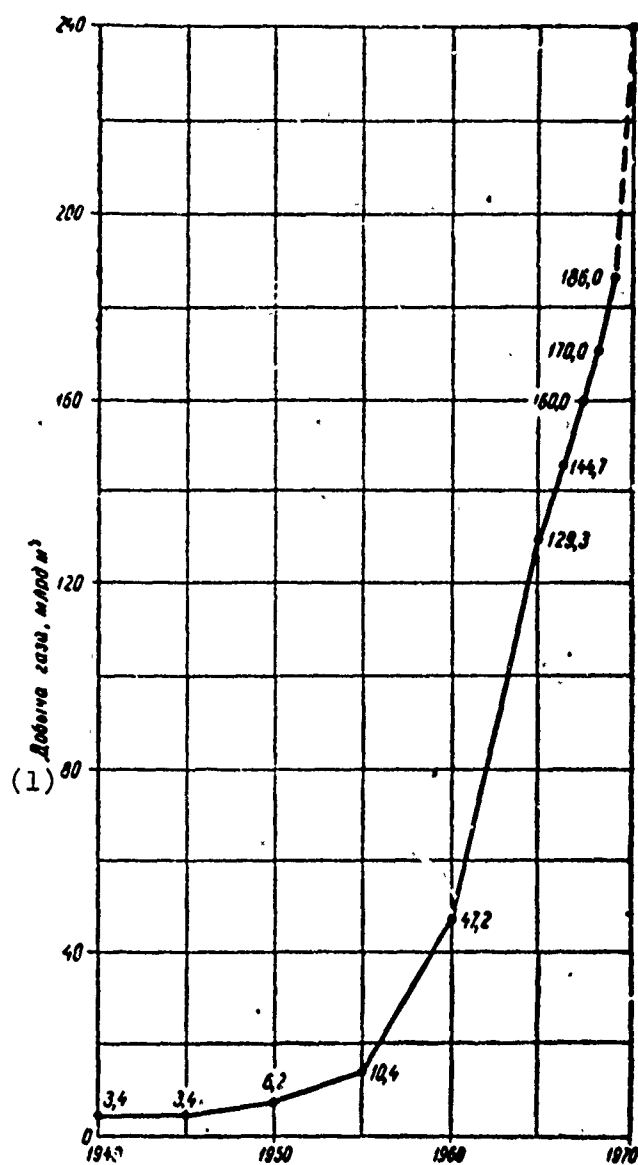


Fig. 1. Growth of extraction of natural gas in the USSR.

KEY: (1) Extraction of gas, billion m³.

Pipeline transport of gas also developed at rapid rates in the period from 1961 through 1967. The total extent of main gas lines grew by 2.5 times and by the end of 1967 comprised 53 thousand km. Underground storage of natural gas grew simultaneously. At the

end of 1967 underground storage areas in water-bearing strata and in exhausted deposits with an active volume of 2.3 billion m³ were being exploited.

It should be noted that the use of natural gas is not always economically advisable. Very small consumers scattered over a wide area are better supplied with compressed gas transported in tanks and bottles. In this connection the basic fuel at present and in the near future for numerous agricultural regions will be compressed gas, whose production is developing at the same vigorous rates as extraction of natural gas.

Still vaster problems will face the gas industry in the future. According to the long-range plan for developing the fuel and energy balance of the USSR, by 1980 the extraction of natural and casing-head gas will comprise about 700 billion m³ per year and their fraction in the total fuel balance will reach 30.3%. Here the plan provides that up to 70-80% of the total extracted fuel will be used in the European portion of the country, while more than 70% of all fuel resources and 75% of the natural gas are concentrated in the eastern regions. The Tyumen' Oblast alone, which contains deposits such as the Urengoy, Zapolyarnyy, and the Medverzhinskoye, unequaled in the entire world, has about half of all predicted reserves of gas. Therefore the XXIII Congress of the CPSU placed upon the gas industry the task of constructing and activating a pipeline from the northern regions of the Tyumen' Oblast into the central and western regions of the country and also of developing a Central Asia-Center pipeline.

Much has been done already. While prior to 1959 pipelines supplying gas to individual regions of the country were constructed, in more recent years large interconnected systems have been developed: Central, Eastern Ukraine, Western, Povolzh'ya, Kavkazskaya, Middle Asia, Ural. A unified system has been

created for control of main gas pipelines which increases the national economic effectiveness of the equipment and also ensures a constant and reliable supply of gas. Figure 2 shows a diagram of the main gas pipelines in the USSR as of the beginning of 1968.

A characteristic feature of the development of the pipeline transport in the USSR is the construction of large-diameter lines, which give huge savings in metal and money because of the huge volume of gas which they carry. In 1967 broad application of 1220-mm diameter pipes was undertaken; pipes of this diameter were used to develop the Middle Asia-Center (2nd line) and the Ukhta-Torzhok pipelines. Pipes with these diameters are not used anywhere else in the world. Preliminary work is already underway on equipping super-capacity gas pipelines from the Urengoy and the Zapolyarnyy deposits to the Center. These gas pipelines will be assembled of tubes 1.4 m and more in diameter and after completion in the middle Seventies will supply up to 150 billion m^3 /year to the European portion of the USSR. By 1980 the quantity of gas transported over these lines to Moscow and other regions of the Center should reach 80-100 billion m^3 /year.

In the longer range the solution is foreseen for the vast problems of transporting gas into the European part of the USSR from the gas deposits in Yakutsk and also in creating a branch system of pipeline in Eastern Siberia and in the Far East.

What are the reasons for the explosive development of the gas industry - what are the advantages of gas over other types of fuel? In order to answer these questions it is sufficient merely to compare the operation of a boiler in which powdered or chunk solid fuel is burned with that of a boiler operating on gas. The basic advantages of gas are immediately obvious. In the first case any areas not accessible for daily cleaning are contaminated with dust; the air of the interior usually contains combustion products

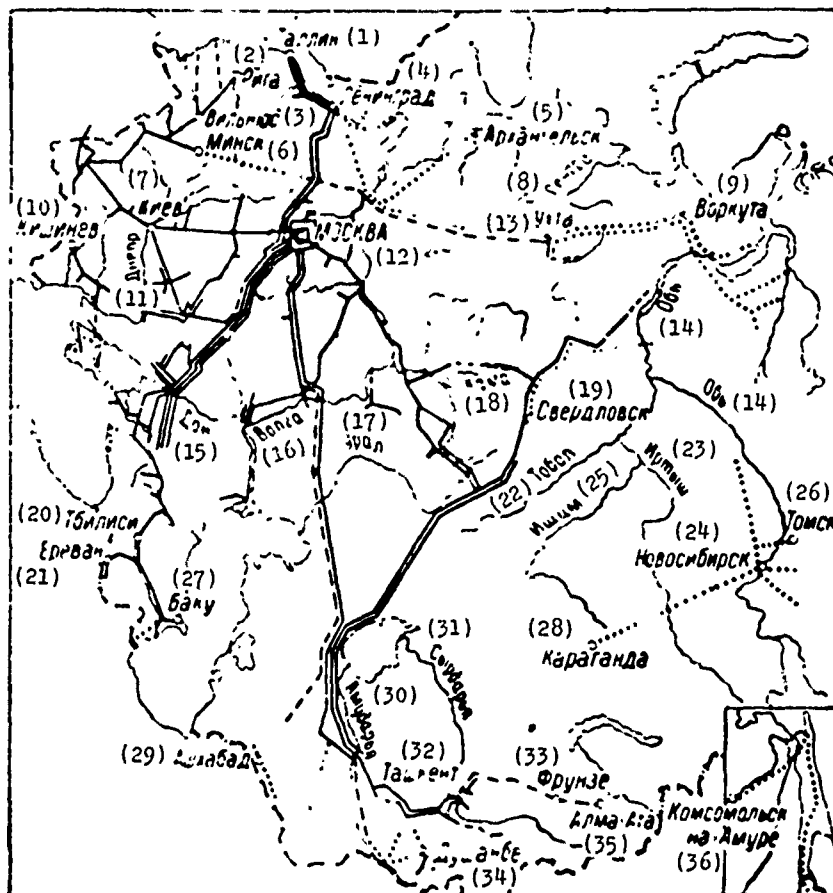


Fig. 2. Diagram of main gas pipelines in the USSR.

KEY: (1) Tallin; (2) Riga; (3) Vilnyus; (4) Leningrad; (5) Arkhangel'sk; (6) Minsk; (7) Kiev; (8) Pechora; (9) Vorkuta; (10) Kishinev; (11) Dnieper; (12) Moscow; (13) Uxta; (14) Ob'; (15) Don; (16) Volga; (17) Ural; (18) Kama; (19) Sverdlovsk; (20) Tbilisi; (21) Yerevan; (22) Tobol; (23) Irtysh; (24) Novosibirsk; (25) Ishim; (26) Tomsk; (27) Baku; (28) Karaganda; (29) Ashkhabad; (30) Amudar'ya; (31) Syrdar'ya; (32) Tashkent; (33) Frunze; (34) Dushanbe; (35) Alma Ata; (36) Komsomol'sk-on-Amur.

harmful to human health. The surrounding area is contaminated with airborne ash, which is unavoidable even with careful cleaning of the stack gases. The systems for supply and preparation of fuel and for removal of ash are complex devices whose servicing requires numerous personnel and frequently requires great physical effort.

The picture in the second case is entirely different. The working area in which the boiler is located is always clean; control of boiler operation, while requiring exact knowledge of the equipment and properties of the fuel itself, is not connected with heavy physical labor and is accomplished under favorable health and hygiene conditions. Instead of cumbersome systems for supply and preparation of fuel, the boiler is equipped with a system of compact gas lines over which gas is supplied and distributed to the boilers in the required quantities. These factors, visible at first glance, do not exhaust the advantages of gas over solid fuel. As indicated by the results of operating identical boilers on solid fuel and on gas, the latter provides better use of the available heat than solid fuel. As a result of conversion of boilers from solid fuel to gas losses due to mechanically-induced incomplete combustion disappear; losses due to chemical incomplete combustion are reduced to a minimum or disappear entirely, while the losses to the escaping gases are reduced. As a result boiler efficiency grows by 2-7% reaching 90-92%. Such high efficiency is impossible when the boiler operates with solid fuel, even when the most economical and technically perfect equipment is utilized.

Finally, the cheapness of natural gas is of enormous significance. This low cost is connected with a very high heat of combustion. The prime cost of gas at the point of extraction averages about 1.2-1.5 rubles/t of ideal fuel (id. f.) while for certain deposits it is even lower. For example, the cost of Uzbek gas is about 0.5 rubles/t, while that for Krasnodar gas is 0.7 ruble/t. In this respect only the cheapest coal in the open

pits of the Kansk-Achinsk Basin (0.8-1.0 rubles/t id. f.) and in the Ekibstuzskiy deposit (1.6 ruble/t id. f.) can compete with gas. The cost of all other fuels is substantially higher, reaching 6.0-6.9 rubles/t id. f. (anthracite and bituminous coal in the Donbass, shaft mining).

The high heat of combustion allows natural gas to compete successfully with other fuels even when transported to regions in which these fuels are extracted over gas lines thousands of kilometers long.

Thus, in all respects gas is a favorable and extremely valuable fuel which permits boiler technology to proceed to a new and higher level. However, it does have its drawbacks. The least bit of carelessness in observing the rules for operating gas equipment or breaking rules of industrial safety can lead to the most severe consequences. Gaseous fuel forms a mixture with air whose explosions are sometimes accompanied by extreme destruction of equipment and even loss of human life. It is clear that the personnel who service gas-boilers, furnaces, and other installations must be highly familiar with the properties of gaseous fuel in order to analyze not only problems of efficiency of their operation but also the questions of industrial safety. Soviet industry already requires numerous cadres capable of correctly servicing gasified installations; in the future this requirement will grow even greater. Therefore the need for broad popularization of accumulated Soviet science and practical information in the field of gas combustion is felt ever more sharply.

Even in its simplest form the combustion of gas is a very complex process, in which various physical and chemical phenomena interweave and compete. It was no accident that the key to understanding it was found by Soviet science as early as twenty and thirty years ago, when Academician N. N. Semenov and other

scientists created the theory of chain reactions and explained the combustion of gas on the basis of this theory. Solution of this problem required the use of very complex mathematical apparatus and experimental methods which were no less complex. However, this does not mean that all of this knowledge is mandatory for a correct knowledge of the properties of a combustible gas and features of its burning, undistorted by excessive simplification. It is sufficient to give careful consideration of the most basic and easily understood laws of nature in order to be able to analyze the essence of these questions. These considerations predetermined the contents of this pamphlet.

The author considers it his pleasant duty to express his gratitude and appreciation to Prof. N. L. Staskevich for the numerous valuable remarks which he made while reviewing the pamphlet.

CHAPTER I

CLASSIFICATIONS AND METHODS OF OBTAINING GAS FUEL

Classification of Gas Fuel

All of the fuel gases which are used in power engineering, industry, public services, and domestically are divided into natural and artificial, in terms of their origin. Natural gases are extracted from the earth's depths, while artificial gases are produced at gasworks or are obtained as the by-product of various technological processes.

In terms of occurrence in the earth, natural fuel gases are divided into gases obtainable from purely gas deposits (usually called *natural* [gaswell] gases) and *petroleum by-product* [casing-head] gases (industrial petroleum gases); these are extracted together with petroleum from petroleum or petroleum-gas deposits.

The artificial fuel gases are divided into various types in accordance with methods of their production. The following are the basic types: *coke* gas, a by-product of the process of dry distillation of bituminous coal; *shale* gas, the basic product of the dry distillation of fuel shales; *producer* gases, obtained by residue-free gasification of various low-grade solid fuels and, in its turn, subdivided into *air-gas*, *water*, *mixed*, and *steam-oxygen* producer gases; *blast-furnace* gas, a by-product of the

process of smelting pig iron from iron ores; oil [petroleum] gas, obtained as the by-product of heat-treatment of petroleum and petroleum products; *liquified* gas which is obtained from natural, casing-head, and artificial petroleum gases from which the light gasoline fraction has been removed and also in the process of stabilization of petroleum and its thermal refining.

The above list does not exhaust the variety of existing fuel gases, but the various types which are not listed here are used as fuel only in small quantities and have no substantial value in the national economy of our country.

The relative role of the enumerated varieties of gaseous fuel in the balance of our country is as follows: natural gases, converted to id. f. (1 kg id. f. corresponds to 7000 Cal) represents more than 70% of the total gas consumption of the country; casing-head and liquified gases represent 9%; the remaining portion is made up mainly of by-product gases from the metallurgical, petroleum, and chemical industries.

The given figures do not pretend to a high degree of accuracy, since from year to year the ratio between the types can change. It should only be noted that the significance of production of special gasworks is continuously being reduced owing to the vigorous growth of extraction of natural gas and also the vigorous development of the metallurgical, petroleum, and chemical industries.

Extraction and Transport of Natural Gas

Like petroleum, natural gases are formed from the residues of plant and animal organisms deposited on the ocean bottom in the form of argillaceous ooze and then subjected to the prolonged action of high-temperature geological and biochemical processes.

The natural gases formed simultaneously with petroleum lie in the depths of the earth together with it, forming oil and gas fields. Some of them, consisting mainly of heavier components, were dissolved in petroleum; another part (the lighter components) is accumulated above the level of the petroleum, forming the so-called gas cap (Fig. 3).

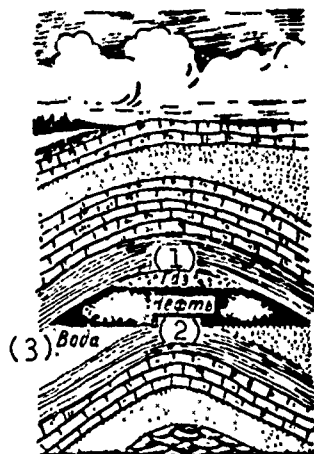


Fig. 3. Gas and petroleum deposit.

KEY: (1) Gas; (2) Petroleum;
(3) Water.

Possessing great penetrating power, natural gases can move in porous minerals (sands, limestone, etc.) for great distances. Accumulating in anticlinal (i.e., convex) folds of these rocks, they form purely gaseous deposits from which natural gases are extracted. Besides this, it can at present be considered as proven that natural gases can be generated in large quantities independently of the formation of petroleum in the process of transformation of organic substances into coal.

The gas-bearing strata and purely gas deposits have a broad horizontal extent and their lower portions are filled with water. Gas accumulations occupy the upper portion of the stratum, pressed by water pressure to the impermeable clay roof above them. For this reason the pressure of the gas depends on the depth at which the level of water which receives the weight of the overlying rocks is located. The density of these rocks is significantly greater than that of water and therefore the formation pressure

substantially exceeds the hydrostatic pressure, which comprises about 1 at. per 10 m. of depth. Thus, at a depth of 1000 m the formation pressure can be significantly greater than 100 at. The gas-bearing strata are located at a great depth - from 700 to 5000 m and more; therefore the formation pressure is usually measured in many hundreds of atmosphere.

In the majority of cases the combustible portion of natural gases from purely gas deposits is made up of methane; however, there are also the so-called gas condensate deposits in which the lightest of the liquid components of petroleum are also found. Such deposits obtain this name because condensates consisting of light gasoline fractions and liquified hydrocarbon gases precipitate out of the gas.

The commercial extraction of natural gas is carried out through specially drilled bores which penetrate to the depth at which the gas-bearing stratum lies. Most frequently used of the many types of drilling are rotary and turbine drillings; electrodrilling has come into wide use recently. During rotary drilling (Fig. 4) a rock bit is rotated from a rotor located on the surface and connected to it by a sectional and gradually extended system of drill tubes. The rock cuttings are brought to the surface by a clay solution [drilling mud] which is brought to the face by a special mud pump and then returned to the surface through the space outside the drill tube. A second purpose of this solution is cooling the bit, and also stiffening the friable walls of the drilling shaft.

The transmission of rotation from the rotor to the bit, which is dropped to the entire depth of the shaft being drilled, is accompanied by major energy expenditures and by distortion of the drilling shaft. In this connection rotary drilling is gradually being replaced by turbine drilling, in which the bit is connected

directly to a turbine through a gear box; the turbine is rotated by means of drilling mud on the face itself. In this system the drill tubes do not rotate and serve only to support the turbo-drill (i.e., a unit consisting of the turbine, gear box, and bit) and to supply the drilling mud.

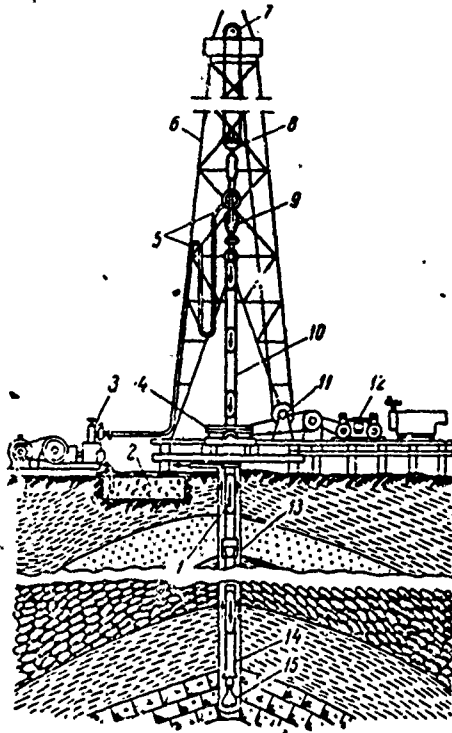


Fig. 4. Schematic diagram of rotary drilling of a shaft. 1 - mud in the drilling shaft; 2 - argillaceous solution [drilling mud]; 3 - mud pumps; 4 - rotor; 5 - flexible mudhose; 6 - derrick; 7 - crown block; 8 - tackle block; 9 - swivel; 10 - square tube; 11 - winch; 12 - motor; 13 - nonrotating tube; 14 - drill pipe [string]; 15 - drilling bit.

During electric drilling the bit is rotated by an electric motor which is also inserted into the drilling shaft with it. The electric motor is supplied by a cable which passes inside the drill string and which is extended as the face penetrates deeper by means of plug connecting couplings.

Upon termination of drilling the drilling tool and the drilling mud are removed and the walls of the shaft are reinforced with casing. For final cleaning to remove drilling mud, rocks, and water the shaft is blown out with gas, after which it is brought into operation.

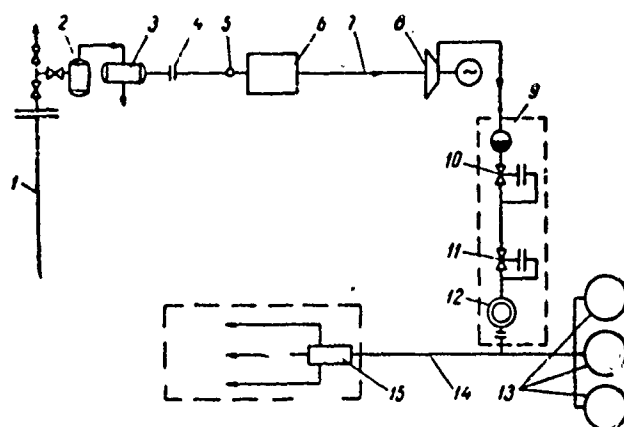


Fig. 5. Schematic diagram of the extraction, purification, transportation, and distribution of natural gas.

1 - well; 2 - primary dust remover; 3 - separator for removal of suspended moisture; 4 - device for measuring gas quantity; 5 - collector for gas from various wells; 6 - device for cleaning and drying the gas; 7 - main gas line; 8 - compressor station [CS] (HC); 9 - gas regulating station [GRS] (ГРП); 10 and 11 - 1st and 2nd stage regulators; 12 - odorizer; 13 - gas-holders; 14 - gas distribution pipeline for feeding gas to establishment; 15 - local gas distribution point [GDP] (ГРП).

Moving out of the well under the action of formation pressure, the gas passes to points for removal of sand, dust, and other substances in centrifugal separators (Fig. 5). After this the gas is dried and if it contains a substantial amount of hydrogen sulfide or carbon dioxide these are removed; this increases its quality and improves transportation conditions. The clean natural gas is sent over a pipeline to the consumers. Every 120-160 km along the pipeline route compressor pumping stations (CS) are installed; at these points the gas pressure is increased. This is necessary to overcome the resistance of the segment of pipeline to the following CS. At the beginning of the segment the gas pressure is 60 at.,

while at the end it is 25 at. Contemporary CS are equipped with powerful rotary compressors driven from gas turbines or electric motors. From the main pipeline the gas passes to gas regulating stations (GRS); these contain filters for cleaning the gas and also pressure regulators and odorizers. In the odorizers a strong smell is added to the gas by the injection of a highly volatile and strongly pungent liquid (the odorant). After this the gas is scattered over distribution lines to the consumers or sent to gas-holders for storage.

The need for the installation of gasholders is dictated by the unevenness of gas load requirements. Ordinary household use has a maximum in the daylight and evening hours; at night it is completely absent. Consumption of gas in heating and ventilation [forced-air heating?] reaches a maximum during winter cold spells, while industrial gas consumption is also uneven due to changes in work at establishments and the periodic nature of technological processes.

To level seasonal oscillations in gas requirements, in recent years ever-wider use is being made of underground storage of gas in spent and water-bearing strata which are well protected by an overhead layer of rock which is impermeable to gas. Gas from main pipelines is brought into these strata through shafts by compressors under a pressure of 50-200 at., depending upon depth. Mechanical impurities are removed from the gas and it is dried during feed from underground storage to GRS.

Collection of Casing-Head Gas In the Oil Field

As was already noted, petroleum in the depths of the earth contains gaseous fuel substances in dissolved form; their content depends on the magnitude of the formation pressure. Usually

200-400 m³ of gas are dissolved in 1 t of petroleum. Petroleum is extracted, like natural gas, through well shafts drilled from the surface to the oil-bearing stratum. Under pressure of the gas cap the petroleum is lifted to the surface, where its pressure is reduced to atmospheric and the solubility of the gases in it is sharply reduced. As a result the gas is separated from the solution and can be used as a fuel.

Separation of petroleum and casing-head gas and removal of petroleum dust from the latter are accomplished in special traps (Fig. 6). For best separation the mixture entering the trap is splashed; for this the trap contains an arrangement of grids, deflectors, plates, and other fittings. A constant level of petroleum is maintained in the trap by means of the lower level regulator, whose float rises when the level increases and opens the valve to the oil escape line through a system of levers. The pressure is maintained in the trap by a counterpressure regulator whose valve is opened by the pressure of the gas; in this case the flow area varies in accordance with the gas flow rate.

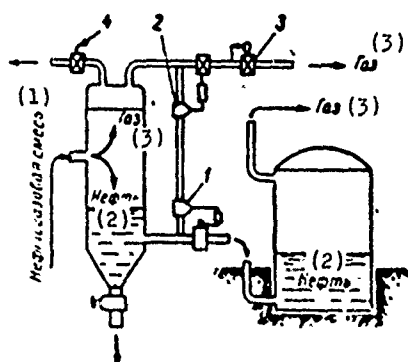


Fig. 6. Diagram of trap equipment. 1 - lower level regulator; 2 - upper level regulator; 3 - counterpressure regulator; 4 - safety valve.

KEY: (1) Oil/gas mixture; (2) Oil; (3) Gas.

If the level of oil in the trap rises to the height of the upper level regulator float despite complete opening of the oil-drain tube valve, the upper level regulator closes its valve to the gas line. With a further increase in oil level the pressure

in the trap begins to rise to a limit beyond which the safety valve opens and oil begins to pour into the drain line. This is connected with loss of gas and light fractions of the petroleum and therefore the safety valve has a signal device to allow service personnel to promptly lower the level of petroleum to the normal height.

To separate the production of high-pressure wells (above 20 at.) a stepwise gas and oil separator is used; a schematic diagram is shown on Fig. 7. The oil/gas mixture enters the high-pressure trap, where mainly the light components (methane and, partially, ethane) are separated from it. Then the oil/gas mixture is directed to medium-pressure traps in which heavier components are separated; after this it passes successively through the low-pressure trap and the vacuum trap for deeper separation of the petroleum and the heavy gases. Pressure is controlled on each stage of separation by appropriate pressure regulators. Part of the gas from the low-pressure trap passes to the separator.

Gas from the high-pressure trap, which does not contain aliphatic components, is sent directly to the consumer after the necessary cleaning and drying. Gases from the medium and low-pressure traps and also gas from the vacuum trap, after passing through the vacuum compressor station, are directed to the gas/gasoline plant for removal of gasoline and liquified gases. The petroleum separated from the gas is directed to field tanks and from there to petroleum refineries.

It should be noted that the collection of casing-head gas can be significantly hampered when wells are scattered over a large area, since the construction of gas lines from each well to the collecting center becomes economically inadvisable. Therefore a certain quantity of casing-head gas is still lost, since it must be burned in torches. Elimination of this loss of casing-head

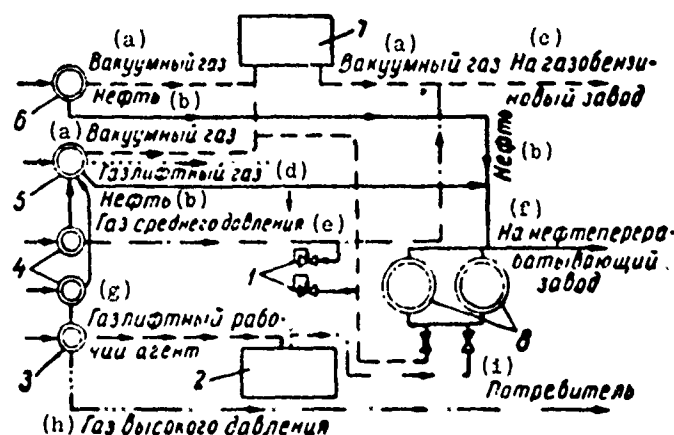


Fig. 7. Schematic diagram of collection of gas on the field. 1 - pressure regulator; 2 - separator; 3 - high-pressure trap; 4 - medium-pressure trap; 5 - low-pressure trap; 6 - vacuum trap; 7 - vacuum-compressor station; 8 - oil-field tanks.

KEY: (a) Vacuum gas; (b) Petroleum; (c) To gas/gasoline plant; (d) Gas-lift gas; (e) Medium-pressure gas; (f) To oil refinery; (g) Gas-lift working agent; (h) High-pressure gas; (i) Consumer.

gas is one of the very central problems which the gas industry is solving at present.

Production of Coke Gas and Shale Gas

If solid fuel is subjected to dry [destructive] distillation - i.e., to heating without access of air - its constituent complex organic compounds are broken down into two parts: volatiles, i.e., gaseous substances and tars, and a solid residue - coke. Depending on the form of solid fuel such decomposition begins at 100-300°C and is completed at 1100-1200°C.

Figure 8 shows the elemental composition of the working mass of solid fuel and depicts schematically the sublimation of

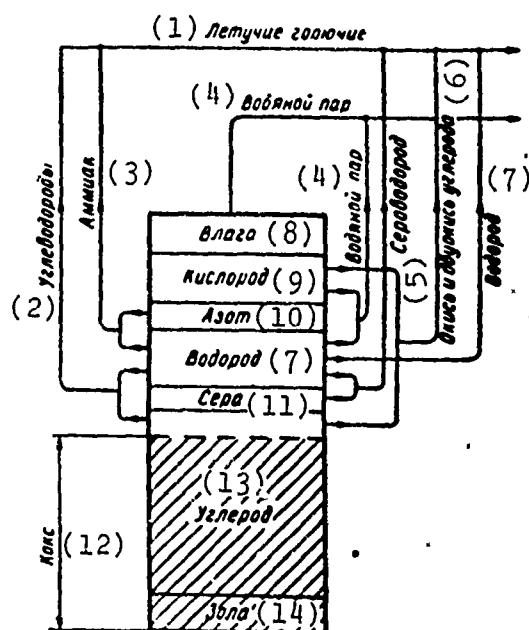


Fig. 8. Diagram of the sublimation of volatiles during dry distillation of solid fuel.

KEY: (1) Volatile fuels; (2) Hydrocarbons; (3) Ammonia; (4) Water vapor; (5) Hydrogen sulfide; (6) CO and CO₂; (7) Hydrogen; (8) Moisture; (9) Oxygen; (10) Nitrogen; (11) Sulfur; (12) Coke; (13) Carbon; (14) Ash.

volatiles during dry distillation. The usual principal goal of this process is production of metallurgical and casting coke. In such cases sintering coals are used as the raw material; coke from these coals has adequate size of individual pieces, high strength, and low abrasion susceptibility. With heating to 350-450°C sintering coals are softened and convert to the plastic state, since the tarry substances contained in the fuel are converted to a liquid. After this the process of decomposition begins; as a result the sintered fuel once again hardens and is converted finally to coke. The sintering coals in our country include certain types of Donets, Kuznets, and Karaganda bituminous coals with volatile yields of 20-27%. In such a process the coke yield comprises 75-82% of the mass of the original coal, while the heat of combustion of the coke gas which is formed comprises 18-25% of the heat of combustion of the initial coal. This corresponds to the production of about 300-350 m³ of coke gas from 1 t of coal.

In those cases when the main purpose of coking is to obtain fuel gas (for example, at gasworks), the above requirements are

not imposed on the obtained coke and we can use as raw material younger noncaking coals which are rich in volatile substances.

The coking process is carried out in furnaces which represent a number of narrow vertical chambers (retorts), with heating channels (verticals) in the partition walls between them. A charge comprised of coals of several types ground to a grain size of less than 3 mm is loaded into the furnace in such a way that a space is left above it for the free passage of volatiles to a stand pipe through which they are pumped from the furnace during coking by an exhaust fan. Then the furnace is sealed closed and the charge is heated without access of air by heat liberated during combustion of heating gas in the verticals.

Coking furnaces operate periodically: the charge is left in them until conversion to coke has occurred, after which it is removed and the furnace is loaded with a new charge dose and a new cycle is begun.

The finished coke, at a temperature of 900-1100°C, is dumped into a special quenching tar and washed with water to prevent combustion in air; the coke is moistened and its temperature is reduced to 100°C and below. The coke gas which is liberated from the charge is pumped out through vertical gas channels (stand pipes) into a gas collector (gas-collecting pipe), from which it is moved on for cleaning. Here it is washed with ammonia water to cool it and for partial precipitation of the tars, after which it is freed from the fog-like content of tar in special tar separators. After this the ammonia and benzene are removed from it. Finally, after additional cleaning to remove hydrogen sulfide and cyanide compounds, followed by drying, the coke gas is sent to a main gas line for distribution among consumers; some of it is used to heat the coke furnace itself. The products which are removed from the coke gas (tar, ammonia, benzene, hydrogen sulfide, etc.) are of

great value as chemical raw materials. After refining they are used in a wide variety of branches of the national economy.

Dry distillation can also be used to obtain fuel gas from other types of solid fuel, in particular from fuel shales. When they are heated without access of air to 1000-1100°C about 75% of the combustible mass is converted into the gaseous state. One ton of fuel shales can yield 350-400 m³ high-quality fuel gas - shale gas - although the content of ash in the initial fuel may amount to 65% and even more.

Shale furnaces are of vertical structure. The charge is loaded from above and the solid residues of the distillation process drop to the bottom. As they are formed they are emptied out from below. Therefore the process in these furnaces is continuous and not periodic, as in the horizontal coking furnaces. All operations relating to charge loading and unloading of solid residues have been mechanized.

The shale decomposition products which are formed in the furnaces are directed through valves of gas outlet lines into a gas collecting pipe and are then sent onward for cooling, cleaning, and drying. Then the shale gas is subjected to compression in compressors and is sent out over the main gas line for transportation to consumers or to gasholders.

Preparation of Producer Gases

Residue-free gasification of solid fuel, usually low-grade fuel, is sometimes used to supply gas for populated areas and industrial enterprises. This same process is also used in motor vehicles and tractors operating in forested regions where they are fueled by chunks of wood instead of gasoline, kerosene, or solar oil.

The process of residue-free gasification consists in the following: a solid fuel is heated to high temperature in the presence of atmospheric oxygen; its combustible part is almost completely converted into a fuel gas, while the solid residue includes only ash (in the form of slag). This marks the principal difference between gasification and dry distillation, since in the latter process the major portion of the combustible mass of fuel is converted into solid residue (coke).

The structures in which residue-free gasification of solid fuels takes place are called gas generators, and the fuel gas obtained in them is called producer [generator] gas.

A gas generator is a high shaft whose walls are lined with refractory brick on the inside. The solid fuel which is to be converted into fuel gas is poured into it from above through a feeder. In the lower portion there is a furnace grate under which an air, steam-air, steam, or steam-oxygen blast is supplied.

Shifting downward along the shaft, the fuel is subjected to the action of the oncoming flow of hot gases; this results in a number of transformations (examined below), while incandescent coke drops out of the furnace grating. Partial combustion of the coke also ensures the necessary heat for the entire gas-generation process. If air is supplied under the grate, carbon dioxide is formed in the combustion zone (along with some carbon monoxide). During its passage through the layer of incandescent coke located immediately above the combustion zone the carbon dioxide is reduced to carbon monoxide. If not only air but also water vapor is supplied under the furnace grating, during interaction with the incandescent carbon it is reduced with the formation of hydrogen.

Along with these basic reactions, processes of thermal decomposition of the fuel occur in the gas generator. As a result

of these reactions methane and other hydrocarbons are formed in some quantity. These reactions occur mainly in the layer of fuel located under the reduction zone. The mixture of combustible and noncombustible gases which is formed (producer gas) is then raised upward where it is cooled, heats the layers of fuel above it, and finally is removed from the upper portion of the gas generator.

Depending upon the nature of the draft, gases of different composition are obtained; in this connection we distinguish air, mixed, water, and steam-oxygen producer gases. Air gas, obtained during the interaction of the carbon in a hot layer of coke with atmospheric oxygen from the air blast, theoretically contains 34.7% carbon monoxide; the remainder is nitrogen. Mixed water-air gas is obtained during reaction of coke carbon with a mixture of air and water vapor. Theoretically it consists of 41% carbon monoxide, 20.9% hydrogen, and 38.1 vol. % nitrogen. In practice the composition of the mixed gas depends on the type of initial fuel and can vary substantially. Water gas is obtained when air and steam blasts are supplied alternately to the gas generator. The air gas which is formed during the period when air is blasted through the gas generator is usually discarded into the atmosphere because of its low value, while the gas obtained in the period of steam blasting (called "water gas") is actually used. Theoretically it consists of equal volume quantities of carbon monoxide and hydrogen and has no noncombustible components whatever. The need for periodic venting with air arises because the reaction between the carbon and the water vapor has an endothermic nature - i.e., it occurs with absorption of heat. Because of this the process of water gas formation gradually weakens and it is necessary to blow air periodically through the layer of hot fuel to intensify the process. The composition of the gas will differ from the theoretical as a function of the type of fuel being converted.

From the technical point of view the most perfect process is the use of a steam-oxygen blast under a pressure on the order of

20 at., which ensures obtaining producer gas with a very low content of noncombustible components. In addition, steam-oxygen gas contains about 10% methane and other hydrocarbons, which means that it has a comparatively high heat of combustion. However, owing to the cost of technical oxygen, from the economic point of view this method is less suitable than the somewhat less perfect but cheaper method examined above.

Producer gases (with the exception of the steam-oxygen blast gas) are not used in pure form for municipal gas supply, since they have a low heat of combustion and are highly toxic due to the carbon monoxide contained in them.

Production of Blast-Furnace Gas

The process of smelting pig iron from iron ores in blast furnaces is accompanied by the formation of a large quantity of combustible gas which is used as fuel under the name "blast-furnace gas."

A blast furnace is a shaft of great height and volume which is loaded from above with successive layers of the initial charge material - fluxed iron ore and coke. Various oxides of iron are used as the iron ore: magnetite Fe_3O_4 , hematite Fe_2O_3 , and brown hematite $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. From the metallurgical point of view the blast-furnace process consists in the reduction of iron from these oxides by coke carbon; from the point of view of heat engineering it represents the residue-free gasification of the coke accompanied by the formation of air producer gas.

The high temperatures required to realize this process are developed through the reaction between the carbon of incandescent coke and oxygen from air heated to 800-950°C which is blown into the furnace at a high rate through tuyeres in the lower portion.

The air blast has to be heated to reach the required intensity of reduction processes. This is accomplished in special air heaters - Cowper stoves.

Close to the tuyeres the gas flow is rich in oxygen. Its reaction with the coke leads to the formation of a mixture of carbon monoxide and carbon dioxide; subsequently, however, as the oxygen is consumed the carbon dioxide is almost completely reduced to CO. Subsequently the high-temperature gas flow is lifted upward and, penetrating through the layers of the charge, it ensures that the reduction of the iron will occur. In the high-temperature regions the process of *direct* reduction occurs; during this the carbon of the coke is oxidized by oxygen from the ferrous oxide FeO. The carbon monoxide which is formed enters the gas flow. Higher, in the zone of relatively low temperatures, *indirect* reduction of the oxygen occurs. This consumes a certain part of the carbon monoxide contained in the gas and it is replaced in the gas flow by carbon dioxide CO₂. A certain portion of the iron is also reduced by hydrogen which is formed during decomposition of water vapor entering the zone of high temperatures with the air blast. The reduced iron is carburized, which transforms it into pig iron; this flows downward and is collected in the hearth from which it is periodically withdrawn through a taphole for further conversion.

The blast-furnace gas which is formed in the furnace leaves it through its upper portion (charge hole). Its composition depends on the quality of the charge, the melting conditions, temperature and humidity of the blast, etc. On the average the combustible portion amounts to only about 30% of the total volume of gas; this portion consists almost wholly of carbon monoxide. In this connection the heat of combustion of blast-furnace gas is not great - from 800 to 960 Cal/m³. This form of fuel has a purely local use, since transporting it over great distances is not economically justifiable. It is used mainly in a mixture with

coke gas, while part of it is used in pure form directly at the metallurgical combine where it was obtained. Uses here include heating of coke furnaces, Cowper blast-furnaces, Martin furnaces, and also for heating steam boilers.

The specific yield of blast-furnace gas depends on the dimensions of the furnace, the quality of the charge, and the operating conditions; it comprises 2500 to 4000 m³ per ton of pig iron

Production of Artificial Petroleum Gases

Petroleum gases are obtained as the by-product of a series of processes in oil refining: straight-run distillation, cracking, pyrolysis, destructive hydrogenation, etc. Petroleum distillation is the process of thermal separation of its fractions (gasoline, kerosene, gas oil, etc.) without appreciable decomposition of the hydrocarbons. Straight-run distillation gas, which is close in composition to the heavy portion of casing-head petroleum gas dissolved in oil, is separated in this process. Straight-run distillation gas contains a large quantity of propane (7-16%) and butane (13-30%); therefore it can serve as the raw material for the production of liquified gas. After separation of these hydrocarbons and gasoline vapors the straight-run distillation gas can be used as a gaseous fuel,

Cracking of petroleum products, the major direction in the contemporary technology of refining petroleum for gasoline and other forms of light fuel, consists in heating the petroleum products to 450-650°C; this results in splitting of the high-molecular hydrocarbons of the initial material with the formation of light hydrocarbons. Naturally, part of the raw material is converted into combustible gas. This process is accomplished both at low pressures - 1-5 at. (vapor-phase cracking) and at high

pressures on the order of 70 at. (liquid-phase cracking). Cracking in the presence of a catalyst is called catalytic cracking, while that without a catalyst is called thermal cracking. These varieties of cracking give different yields of light petroleum products and gas. In most cases the obtained gas is distinguished by high content of unsaturated (olefinic) hydrocarbons which represent a valuable raw material for a number of chemical production processes and are separated from this gas before it is used as a fuel.

The pyrolysis of petroleum products consists in heating them up to 650-750°C at atmospheric pressure for the purpose of obtaining aromatic hydrocarbons (benzene C_6H_6 and its homologs) and also olefines (ethylene C_2H_4 , propylene C_3H_6 , butylene C_4H_8 , etc.). Kerosene is the most frequent object of pyrolysis. In this process the yield of gas reaches up to 50% of the mass of initial raw material and, like its composition, depends strongly on the nature of the raw material and the process temperature. After removal of aromatic and olefinic hydrocarbons pyrolysis gas can be used as a fuel.

Catalytic cracking which is accomplished in the presence of hydrogen at high pressure (500-700 at.) is called destructive hydrogenation. In this process not only are high-molecular hydrocarbons split, but the hydrocarbon molecules are enriched with hydrogen atoms. For example, a molecule of the unsaturated hydrocarbon ethylene C_2H_4 is converted into the saturated hydrocarbon ethane, C_2H_6 , by the attachment of a hydrogen molecule H_2 to it.

Destructive hydrogenation is an extremely advanced process which makes it possible to refine heavy liquid fuels into light fuels, while simultaneously obtaining a large yield of gaseous fuel. Thus, from the heavy residues of straight-run distillation of petroleum (mazut) it is possible to obtain up to 85-87% automotive gasoline and 13-15% combustible gas.

Production of Liquified Gases

The basic source for production of liquified gases is found in those natural and artificial gases which in unrefined form contain a significant quantity of heavy hydrocarbons (ethane, propane, butane, etc.). Such gases are called "aliphatic." These include casing-head petroleum gases, natural gases from gas-condensate deposits, petroleum gases from straight-run distillation and from cracking and pyrolysis of petroleum products, and also gases obtained by destructive hydrogenation of solid and liquid fuel.

Before any of the gases listed above are used as a fuel they are subjected to stripping. This operation consists in the removal of components of raw unstable gasoline from aliphatic gas by compression, absorption, or adsorption. The simplest method is compression. It is based on the fact that when gas is compressed the partial pressures (see Chapter II) of the components to be removed from it are raised to such a degree that they are condensed and are drawn off in liquid form.

Figure 9 shows the diagram of two-stage compression. Refined aliphatic gas enters the first stage of the compressor; here it is compressed to 6 at., after which it is passed through cooler 1 into separator 2. Here separation of the heaviest gasoline fractions occurs. After separation of these fractions the gas passes through receiver 3, which balances the operation of the installation, and is directed to the second compressor stage where it is compressed to 16-40 at.; it then goes through cooler 1 into separator 2. From here the stripped gas is drawn off for use as a fuel.

The absorption method consists in the removal of heavy hydrocarbons from the gas by their absorption by a liquid, while the

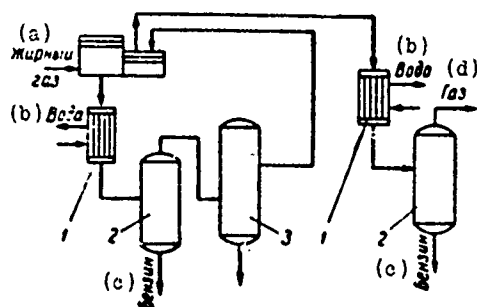


Fig. 9. Schematic diagram of two-stage compression. 1 - cooler; 2 - gas separator; 3 - receiver.

KEY: (a) Aliphatic gas; (b) Water; (c) Gasoline; (d) Gas.

adsorption method consists in their adsorption on the surface of solid materials (most frequently activated charcoal).

The second stage in the production of liquified gases is stabilization of the raw gasoline (separation into individual fractions). The diagram of the simplest stabilization installation on which stable gaseous gasoline and liquified gas (predominantly a propane-butane mixture) are obtained is shown on Fig. 10. Unstable gasoline passes under a pressure of 10-15 at. into heat exchanger 1, where it is heated to 40-45°C; it is then directed into the middle portion of column 3. In the upper portion of the column the vapors of the propane-butane mixture are drawn off; this mixture is then converted into a liquid and cooler-condenser 4 and then collected in collector 6. From here a part of the propane-butane mixture is fed by pump 5 for column reflux, while part of it is directed to receiving tanks. Stable gasoline passes from the bottom of the column first through heater 2 and then through heat exchanger 1, after which it is sent to storage. More complex stabilization installations ensure separation of fractions removed from the gasoline into individual hydrocarbons with purity up to 98%.

In those cases when gases containing a significant quantity of unsaturated olefinic hydrocarbons are subjected to stripping, during stabilization of the gasoline saturated and unsaturated components are separated either indirectly or during subsequent

chemical refining. Unsaturated hydrocarbons (propylene and butylene) are used subsequently as raw materials for the production of plastic, while the saturated hydrocarbons (propane and butane), which in these cases represent production wastes, are used as fuel.

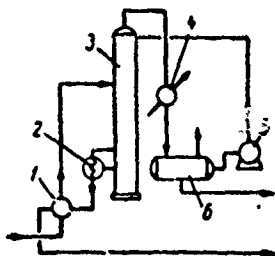


Fig. 10. Diagram of the simplest stabilization installation.

CHAPTER II

THE PHYSICAL PROPERTIES OF GASEOUS FUEL

Particular Features of the Gaseous State

In order to shatter a rock with a hammer it is necessary to expend a large amount of force. Why? Indeed, because the individual molecules of which the rock consists hold strongly to one another and, in order to break it apart, it is necessary to overcome the forces of mutual attraction between the molecules.

All bodies in nature are attracted to one another. This includes the planets of the Solar System, which rotate around the Sun because invisible threads of mutual attraction hold them together, preventing them from flying off in all directions. This also relates to the molecules of which all physical bodies consist.

The force of mutual attraction between molecules is proportional to the distance between them and is sharply reduced with an increase in this distance. The properties of all physical bodies depend on the average distance between molecules. In solid bodies these distances are very small and therefore their molecules hold very strongly to one another. This leads to the basic property of solid bodies: constant shape and constant volume. However, this is explained not only by the small distance between molecules but also by the fact that the molecules possess

a relatively small reserve of energy. Let us imagine that some small sphere is held in arbitrary position by elastic (for example, rubber) threads which are stretched in various directions. If we pull the sphere toward us, overcoming the resistance of the threads, and then let it go it begins to oscillate around its middle position, with this oscillation being the more intensive the stronger the force with which it was pulled. The motion of each molecule of a solid body has a similar nature; the molecule is held by forces of attraction of neighboring molecules acting from all sides. The reserve of energy possessed by individual molecules is relatively small and it is inadequate to tear them away from one another.

Heating a solid body leads to an increase in the energy reserve in its molecules, so that the intensity of their oscillatory motions grows until the forces of mutual attraction are no longer sufficient to hold the molecules in a certain middle position. In this case the solid body melts, i.e., it is converted into a liquid whose molecules are distinguished by a much greater mobility and can be displaced with respect to one another. This is the definition of the basic property of liquids - they possess fluidity. Nonetheless liquids, like solid bodies, retain a constant volume. There is not a sufficient energy reserve in their molecules for them to become completely detached from the other molecules.

Heating of a liquid leads to a situation in which it finally begins to boil and is transformed to vapor, i.e., it converts into the gaseous state. This means that the reserve of energy of the molecules is increased to such a degree that the molecules overcome the force of mutual attraction and fly away from one another. Therefore with respect to the behavior of molecules and, consequently, in terms of physical properties gases differ radically from solids and liquids. Possessing a large energy reserve, every molecule of a gas moves uniformly in a straight

line until it collides with another such molecule. After a collision the molecules fly off in directions conditioned by the direction and force of the impact and continue their motion from one collision to another. The average distance between molecules in gases is so great as compared with the dimensions of the molecules themselves that the forces of mutual attraction are virtually nonexistent and have no influence on the nature of this motion.

A gas which is enclosed in any certain vessel can be compared to an empty space in which a numberless set of elastic balls is borne in chaotic disorder; the balls are continuously colliding and exchanging energy. Such a presentation permits us to understand just why gas tends to extend uniformly to fill the entire space available to it, however great this volume may be. In this property of gases we find the basic distinction between them and solid and liquid bodies.

Basic Parameters of a Gas

The greater the reserve energy which the molecules of the gas possess, the more intensive their motion and the greater their average velocity. The degree of intensity of motion of molecules of a gas is characterized by its *absolute temperature*. Although the absolute temperature is measured in degrees and not in units of energy measurement, actually for gas it is a measure of its internal (thermal) energy - i.e., the energy of motion of the molecules which comprise it. Thus, if the average velocity of molecules of a gas grows, let us say, by two times, their total energy of motion is increased by four times (proportional to the square of the velocity) and the absolute temperature of the gas is increased by four times. If we imagine a gas whose molecules are immobile, i.e., have absolutely no energy reserve (this case is impossible in reality), its absolute temperature will equal zero. Thus, the absolute temperature of the gas can be character-

ized as the measure of the intensity of chaotic motion of its molecules. Absolute temperature is measured in degrees Kelvin ($^{\circ}\text{K}$).

The temperature scale which is accepted in international technical practice (on it the temperature is expressed in degrees Celius - $^{\circ}\text{C}$) makes it possible to use a thermometer to determine not the absolute temperature of a gas, but only the excess of its temperature above that corresponding to the melting point of ice. The absolute temperature of ice at which it begins to melt equals 273.15 K or 0°C . Therefore in order to determine the absolute temperature of a gas it is necessary to add 273.15 to the reading of a thermometer in degrees Celius¹. For example, if a reading of 27°C is obtained during measurement of the temperature of the gas and then the thermometer reading is increased to 327°C after the gas is heated, we can assert that the absolute temperature of the gas was doubled during heating (i.e., from 300 to 600°K) and consequently the energy reserve for motion of its molecules was also doubled.

As a formula the connection between the absolute temperature T in $^{\circ}\text{K}$ and the temperature t measured on the international scale in $^{\circ}\text{C}$ is expressed by the equality $T = t + 273.15$ or $t = T - 273.15$.

Owing to the chaotic nature of their motion the molecules of the gas tend to fly off in all directions. This does not occur only until such time as the gas is enclosed in a vessel with adequately strong and dense walls. The result of collision of gas molecules over the inner surface of the vessel walls and on the surface of bodies located inside the gas is reflected in the fact that a gas exerts a certain *pressure* on all surfaces

¹ In practical measurements the 0.15 is disregarded - i.e., 273 is the amount added.

with which it is in contact. If the walls of the vessel are not sufficiently strong it can be destroyed under the pressure of the gas. Therefore the natural unit of measurement of pressure is the force exerted per unit surface. In practice force is measured in kilograms force (kgf, or kG) while the surface is measured in square meters (m^2); therefore the unit of pressure measurement is a force of 1 kgf acting on a surface of $1 m^2$, i.e., $1 \text{ kgf}/m^2$.

This unit is small and therefore is not always convenient for practical application. In practice pressure is most often measured in technical atmospheres (at), where $1 \text{ at} = 10,000 \text{ kgf}/m^2$. Another frequently-used unit is 1 mm Hg, equal to $13.6 \text{ kgf}/m^2$. This term derives from the fact that because of its weight a column of mercury 1 mm high exerts a pressure at its base equal to $13.6 \text{ kgf}/m^2$. A third and no less useful unit of pressure measurement in the study of gases is 1 mm H_2O , which is equal exactly to $1 \text{ kgf}/m^2$ in value. In actual fact, this is another name for the same unit of pressure measurement.

The atmospheric shell which surrounds the terrestrial ball exerts a pressure on all objects on it; this pressure is called atmospheric. This pressure is measured by a barometer and therefore is called a barometric pressure. If a gas is located in a vessel surrounded by the terrestrial atmosphere, its pressure on the internal walls of the vessel may be greater or less than barometric. In the first case the difference between the pressure of the gas in the vessel and the pressure of the surrounding atmosphere tends to stretch and break apart the walls of the vessel. This difference is called the *excess* pressure of the gas. The instruments with which excess pressure is measured are called *manometers*. In the second case the difference between the barometric pressure and the pressure of the gas in the vessel tends to compress and crush in the walls of the vessel. This difference is called the *rarefaction*. The instruments used to measure

rarefaction are called vacuum gauges. In boiler practice it is necessary to deal with minor rarefactions (in the furnace, in chimneys, etc.). The instruments used to measure such small rarefactions are called *draft gauges*.

To determine the *absolute* pressure of a gas in a vessel (bottle, gas holder, pipeline, etc.) it is necessary to add the magnitude of the barometric pressure to the manometer reading or subtract the reading of the draft gauge or vacuum gauge from the barometric pressure. Barometric pressure varies somewhat as a function of weather and altitude above sea level; during normal weather at sea level it equals 760 mm Hg or 1.033 at (1 atm = a physical atmosphere). Such a pressure is called the normal pressure. In practice the oscillations of atmospheric pressure will be minor; therefore it can roughly be considered to equal 1 at. The letter *p* is the accepted designation for pressure of a gas.

We already know that every gas, in view of the peculiarities of its molecular structure, strives to expand infinitely. Therefore to form a judgment on the quantity of gas it is not enough to know the volume which it occupied. This requires also knowledge of its *density* or *specific volume*. The density of a gas is the name given to the mass per unit volume (1 m³) of the gas, expressed in kilograms of mass. The specific volume is the reciprocal of density - i.e., the volume which is occupied by 1 kg of a given gas.

$$\rho = \frac{m}{V};$$

$$v = \frac{V}{m},$$

where ρ is the density of the gas in kg/m³; m is the mass of the gas kg; V is the volume of the gas, m³, and v is the specific volume of the gas, m³/kg.

It is obvious that

$$p = \frac{f}{r}.$$

The quantities examined above - temperature, pressure, and specific volume (density) - are called the *basic parameters* of the state of the gas and serve to completely characterize the physical state of a gas.

The Laws of Ideal Gases

What will happen if a gas which is enclosed in a bottle with strong walls is heated to a higher temperature? In order to answer this question we will attempt to use the ideas which we have already presented on the physical peculiarities of gases. It is obvious that the volume of the gas will remain unchanged; this is why it is placed in a strong bottle. The rate of motion of its molecules would increase; therefore there should be a corresponding growth both in the force of their impacts on the walls of the bottle and in a number of such collisions. We will assume that the average velocity of molecules of a gas grows by two times. Then the force of each impact will also increase by two times and the quantity of impacts will also double. Consequently, the pressure of the gas will grow by 4 times - i.e., in proportion to the square of the average velocity of motion of the molecules. And we already know that in order for this velocity to be increased by two times the absolute temperature of the gas must grow by 4 times. Thus, the pressure of the gas is increased by the same number of times as its absolute temperature is raised. Generalizing this simple judgment, we can formulate one of the most important laws of the state of gases: *in the same volume the absolute pressure of a gas varies in direct proportion to its absolute temperature*. This law is called Charles' law and as a formula is written in the form of the equality

$$\frac{p_1}{p_2} = \frac{T_1}{T_2}, \quad (1)$$

where p_1 and p_2 are the initial and final absolute pressures of the gas, while T_1 and T_2 are its initial and final absolute temperatures.

Example 1. A manometer on a bottle containing a gas shows a pressure of 1 at. The thermometer shows the temperature to be 27°C . What pressure will the manometer show if the gas in the bottle is heated to 327°C ?

Do not forget that our instruments show not the absolute but relative parameters. The absolute pressure of the gas in the bottle before heating will be 1 at greater than that shown by the manometer - i.e., $p_1 = 1 + 1 = 2$ at. The absolute temperature of the gas before heating will be $T_1 = 27 + 273 = 300^\circ\text{K}$. After heating $T_2 = 327 + 273 = 600^\circ\text{K}$, i.e., it will be doubled. According to equality (1) the absolute pressure of the gas should be increased by the same number of times, i.e., $p_2 = p_1 T_2/T_1 = 2 \cdot 600/300 = 4$ at. The manometer shows not the absolute pressure, but the excess pressure. Consequently it will read 1 at less - i.e., 3 at.

We will now examine a somewhat more complex case. A gas is enclosed in a cylinder with a piston and can be expanded or compressed in such a way that its pressure will remain constant. For this the piston should be loaded by some constant load (Fig. 11).

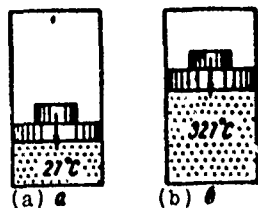


Fig. 11. Change in the volume of gas during heating and with a constant pressure: a - gas prior to heating; b - gas after heating.

When the gas is heated the average velocity of motion of molecules is increased; consequently the force of their impacts on the walls will grow. In order for the pressure to remain constant, the frequency of these collisions should be reduced by the same factor as the above increase. With a growth in the velocity of motion of the molecules the frequency of impacts remains constant if the volume of the gas is increased in direct proportion to this velocity, and it will be decreased (by as many times as the velocity is increased) if the volume is increased in direct proportion to the square of the velocity of motion of the molecules - i.e., in direct proportion to its absolute temperature. Thus, with heating from 27 to 327°C (at constant pressure), i.e., when its absolute temperature is doubled (from 300 to 600°K), the volume of the gas will also be doubled.

By generalizing this reasoning we can formulate the second of the most important laws of the gaseous state: *at constant pressure ($p = \text{const}$) the volume of the gas (or its specific volume) will vary in direct proportion to its absolute temperature, while density will vary inversely to it.*

This law is called the *Gay-Lussac law* and as a formula is written as the following equation:

$$\frac{V_1}{V_2} = \frac{T_1}{T_2}, \quad \text{or} \quad \frac{\rho_2}{\rho_1} = \frac{T_1}{T_2}, \quad (2)$$

where V_1 and V_2 are the initial and final volumes (specific volume) of the gas; ρ_1 and ρ_2 are the initial and final densities of the gas; T_1 and T_2 are the initial and final absolute temperatures of the gas.

Example 2. The temperature of air entering an air heater to be warmed by a blast fan is 27°C, while at the output from the heater it equals 327°C. By how many times is the rate of

motion of the gas increased if the input and output fittings of the air heater have identical dimensions?

The absolute temperature of the air at the inlet to the heater is $T_1 = 27 + 273 = 300^\circ\text{C}$, while at the output it is $T_2 = 327 + 273 = 600^\circ\text{C}$. The volume of the air leaving the heater is $V_2 = V_1 T_2/T_1 = V_1 \cdot 600/300 = 2V_1$, i.e., it has been increased by a factor of two. And since the areas of the inlet and outlet fitting sections are identical, the speed of air in the outlet fitting will be double that at the inlet.

We will now assume that at constant temperature the absolute pressure on a piston above the gas is doubled. Since the temperature of the gas remains unchanged, the force of impacts of molecules on the walls of the cylinder also is unchanged. This is possible only when the frequency of the collisions is doubled - i.e., when the volume of the gas has been halved as compared with the initial value.

Generalizing the above, we arrive at the third of the basic laws of the gaseous state: *at a constant temperature the volume (or specific volume) of a gas varies inversely to the absolute pressure of this gas, while the density is directly proportional to its absolute pressure.*

We can also say that *if the volume of the gas is changed while the temperature remains the same the change in the pressure will be inversely proportional to the volume.*

This law is called *the Boyle-Mariotte law* and as a formula is expressed by the equality:

$$\frac{V_1}{V_2} = \frac{p_2}{p_1}, \text{ or } \frac{\rho_2}{\rho_1} = \frac{p_1}{p_2}, \quad (3)$$

where V_1 and V_2 are the initial and final volumes (specific volumes) of the gas; ρ_1 and ρ_2 are the initial and final densities of the gas; p_1 and p_2 are the initial and final absolute pressures of the gas.

When we are using gas to heat steam boilers or for any other requirements, we first of all must know just how great a quantity of gas we are using. The accepted unit of weight measurement - the kilogram - is inconvenient in gas-use practice. It is obvious that in this case a volume unit - the cubic meter (m^3) - is a far more convenient unit of measurement. However now another difficulty is encountered: 1 cm^3 can contain different quantities depending on its pressure and temperature. For example, if in one case the absolute pressure of the gas equals 10 at and in the second case 1 at, 1 m^3 in the first case will contain 10 times more gas than the cubic meter in the second case (at identical temperatures). In exactly the same way, if the pressures are identical and in one case the temperature equals 27°C and in the other case 327°C, 1 m^3 in the first case will contain double the amount of gas as in the second case, since the absolute temperature (and therefore the specific volume) will be halved in the second case.

In order to eliminate this ambiguity it is necessary to reduce the volume of gas to the so-called "normal conditions" - to normal temperature (0°C) and normal pressure (760 mm Hg). This means that the quantity determined is that volume which a given gas would occupy if its pressure and temperature were normal. Reduction of a volume of gas to normal conditions can be carried out through the following formula, which unites the Boyle-Mariotte and the Gay-Lussac laws;

$$V_0 = V \frac{p T_0}{p_0 T}, \quad (4)$$

where V_0 is the volume of gas in m^3 under normal conditions (p_0 and T_0); V is the volume of gas to be reduced to normal conditions with the parameters p and T .

We will substitute the values of p_0 and T_0 into formula (4)

$$V_0 = V \frac{p \cdot 273}{760T} = V \frac{p}{760} \cdot \frac{273}{t+273}, \quad (5)$$

where t is the temperature of the gas, $^{\circ}\text{C}$.

Example 3. A gas occupies a volume of 100 m^3 at an absolute pressure of 5 at and a temperature of 273°C . Reduce its volume to normal conditions.

We will solve the example by using formula (5). During the derivation of formula (5) the value of p_0 was stated in mm Hg. Therefore during solution of the example p should be established in these same units. The absolute pressure at 5 at equals $760 \times 5 \text{ mm Hg}$:

$$V_0 = 100 \frac{760 \cdot 5}{760} \cdot \frac{273}{273+273} = 250 \text{ m}^3.$$

If volumes of gas are given under normal conditions in practical measurements, by comparing them with each other we can immediately state which of them contains more gas and how many times more. Thus, a cubic meter of gas reduced to normal conditions is the quantity of gas which will occupy a volume of 1 m^3 under normal conditions. It represents a very convenient unit for measuring quantity (not volume!) of a gas and is used as such in all cases when it is necessary to deal with gas in its ordinary (not liquified) state.

Occasionally, for example during calculations of gas from gas-supplying organizations, the quantity of gas is measured not under normal conditions but under standard conditions. There is no difference in principle here, but the volume of gas in this case is reduced to 760 mm Hg. and a temperature of 20°C (standard temperature).

All molecules of one and the same gas have identical structure, and therefore they also have identical weight. The weights of molecules of different gases are different. To compare them with one another we can use the concept of *molecular weight*. Historically the concept of molecular weight of a gas is made up of the ratio of absolute weight of one molecule of a given gas to the absolute weight of one atom of the lightest of gases existing in nature - hydrogen. For oxygen this ratio comprises approximately 31.9. It is more convenient to take the molecular weight of oxygen as exactly equal to 32. Then the molecular weight of hydrogen is found to equal 2.016 (one molecule of hydrogen consists of two atoms), while the weight of nitrogen is 28.016, carbon monoxide 28.010, methane 16.043, carbon dioxide 44.020, etc. Knowledge of these values makes it possible to establish the degree to which the molecules of one gas are lighter or heavier than molecules of another gas.

We will now compare two different gases under identical temperatures and pressures occupying identical volumes. We will assume that the molecules of the first gas are 4 times heavier than the molecules of the second gas. Since the temperatures of the gases are equal and, consequently, the energy of motion of their molecules is equal, the speed of motion of molecules of the second gas will be twice as great as the speed of motion of the first gas. This means that the force of impact of molecules on the walls, directly proportional to the weight of the molecule in its velocity, will be half as great in the first gas as in

the second. But the pressures of the two gases are identical. Consequently, the frequency of molecule impacts on the wall should be half as great in the first gas as in the second. It is easy to see that this condition will be met only when the total number of molecules in the first gas is the same as the total in the second gas.

Generalizing this reasoning we arrive at a conclusion which represents yet another of the most important gas law: *different gases under identical conditions of temperature and pressure and occupying equal volumes contain equal numbers of molecules.*

On the basis of this law, which is called *Avogadro's law*, we can assert that the weight of different gases occupying identical volumes and under identical temperatures and pressures are related to one another as their molecular weights. For example, if oxygen and hydrogen are enclosed in bottles of equal volume, if temperature and pressure are equal the oxygen will weight 16 times more than the hydrogen.

This same position can also be expressed in this way: if the weight of different gases under identical temperatures and pressures are related to one another as their molecular weight, the volumes of these gases are identical. This leads to the possibility of introducing still another unit of measurement for the quantity of a gas, a unit which is very convenient in practice - the kilomole (komole). A kilomole of a gas is the name given to that quantity of it whose weight in kilograms is numerically equal to its molecular weight. Thus, one kmole of hydrogen weighed 2.016 kg, 1 kmole of oxygen weighs 32 kg, etc. The volume of 1 kmole of a gas is called its molar volume. On the basis of the above the molar volumes of the different gases are identical at equal temperatures and pressures. In particular, under normal conditions the molar volumes of all gases equal

22.4 m³/kmole. This quantity allows us to find the specific volume and density for any gas under normal conditions if this molecular weight is known:

$$v_0 = \frac{22.4}{\mu} [\kappa^3/\kappa_0]; \quad \rho_0 = \frac{\mu}{22.4} [\kappa_0/\kappa^3]. \quad (6)$$

where v_0 and ρ_0 are the specific volume and density of the gas at normal conditions; μ is the molecular weight of the gas.

The laws examined above would be strictly valid only if the molecules of gas represented material points - i.e., if they possessed a mass intrinsic to them and were completely without volume. Furthermore, forces of molecular adhesion would be absent. In other words, these laws relate not to [gases] which exist in nature, [but to] idealized models of gaseous bodies - "ideal gases." In all gases which exist in nature the molecules have a finite volume (however small) and forces of molecular adhesion do exist, although extremely small. Therefore when applied to these gases the laws of ideal gases give a certain degree of error. It is true that this error is very small. For the majority of gases used in technology, having low molecular weights (approximately to 30), this error can be ignored. The best illustration of this position is the fact that the first laws for ideal gases were obtained experimentally in studies conducted with gases which actually exist in nature. Thus the law of inverse proportionality between pressure and volume of a gas at constant temperature was discovered in 1661 by the English physicist Robert Boyle. At that time there was as yet no clear presentation of the nature of the gaseous state of bodies, there was no kinetic theory of gases, and therefore there is no question that this discovery was of a purely experimental nature.

Gaseous Mixtures and Their Volume Composition

If the basic features of the molecular structure of gases are known, it is easy to imagine just what occurs if several different gases are placed in one and the same vessel. Actually we know that the freedom of displacement of each molecule of each gas inside the vessel is in no way limited. Consequently, each of the gases is distributed uniformly throughout the entire volume of the vessel - i.e., its concentration (number of molecules per l^3 of volume) will be identical at all points in the volume of the vessel. Several different gases placed in one of the same vessel form a uniform mechanical mixture which is characterized by equality of concentration of each of the components throughout the entire volume of the mixture.

It is true that under terrestrial conditions, when the force of gravity is operative, the uniformity of distribution of different gases in a mixture is somewhat disrupted: the heavier molecules will be drawn more strongly toward the lower portion of the vessel, while the lighter ones will be drawn to the top. But in practice the action of the force of gravity is negligibly small and such differences in the composition of the mixture at different heights should not be noticeable. The air of the terrestrial atmosphere, consisting mainly of two gases - nitrogen and oxygen - serves as an adequate example. Although the molecules of oxygen are somewhat heavier than the molecules of nitrogen, their distribution in the atmosphere (or in any case in its dense layer) is completely uniform.

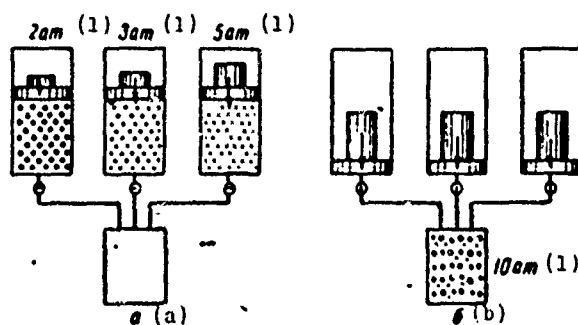


Fig. 12. Partial pressures of components of a gaseous mixture: a - prior to mixing; b - after mixing.
KEY: (1) at.

We will assume that different gases are placed in cylinders of identical volume (Fig. 12a) and with equal temperature, but different absolute pressure: 2, 3, and 5 at respectively. We will assume further that all three cylinders are connected by pipes with a fourth cylinder of the same volume but which contains no gas of any kind. Each tube is equipped with a valve. We will pass the gas from the first cylinder into the fourth by opening the valve and lowering the piston to the bottom. Since the volumes of the first and fourth cylinders are identical, the number and force of collisions of molecules of the first gas will remain the same in the fourth cylinder as they were in the first; therefore the pressure in it will also equal 2 at. By the same procedure we will now pass the gas from the second cylinder into the fourth. The number and force of collisions of molecules of the second gas will remain the same in the fourth cylinder as they were in the second; consequently, the pressure of the second gas will remain as before. However, it is added to the pressure of the first gas and consequently the total pressure in the fourth cylinder will equal 5 at. After transfer of gas from the third cylinder the total pressure in the fourth cylinder becomes equal to 10 at (See Fig. 12b)

Thus, we arrive at the conclusion that each of the components of the gaseous mixture renders the same pressure on the walls of the vessel containing the mixture as it would render on it if it were alone in the vessel, separated from the other components. This pressure is called the *partial pressure of the component*. The second conclusion from our reasoning is that *the pressure of the gaseous mixture will equal the sum of the partial pressures of its components*. This position (*Dalton's law*) represents the basis for all of our concepts regarding gaseous mixtures. Dalton's law is expressed by the equality

$$P_{\text{cm}} = P_1 + P_2 + \dots + P_n. \quad (7)$$

where p_{cm} is the pressure of the mixture of gases; p_1, p_2, \dots, p_n are the partial pressures of the 1, 2, ..., n-th components of the mixture.

We will now once again assume that the components of our mixture are located in separate cylinders and that the pressure of each is as before (Fig. 13z). We desire now that the pressure in each of them be brought equal to the pressure of the mixture (i.e., 10 at) while the temperature must remain constant. To accomplish this it is necessary to move the pistons downward to reduce the volume of each component by as many times as the factor by which we wish to increase the pressure; by 5 times for the first component, $10:3 = 3.33$ times for the second, and 2 times for the third (Fig. 13b).

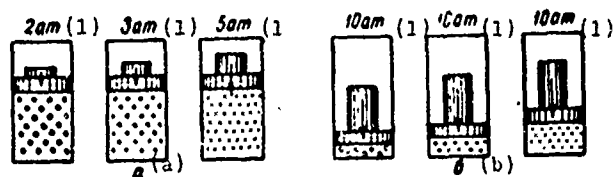


Fig. 13. Reduced volumes of components of the gaseous mixture: a - components occupy the entire volume and have their own partial pressure; b - components have the pressure of the entire mixture and occupy their reduced volume.

KEY: (1) at.

A volume occupied by a component of a gaseous mixture at the pressure and temperature of the mixture but when it is separated from the other components it is called the *reduced* volume of this component. In our case the reduced volume of the first component will equal 0.2, that of the second component 0.3, and that of the third 0.5 of the initial volume. From this an important conclusion is drawn: *the volume of a gaseous mixture equals the sum of the reduced volumes of its components.*

Gases can be mixed in various proportions and therefore different mixtures containing the same components may have different compositions. Consequently in order to characterize a gas mixture it is not sufficient to know its components. It is necessary to also know the proportion of these components in the mixture. Here we will turn for help to the concept of reduced volume of a component. It is obvious that the larger the quantity of any component in the mixture composition, the greater will be its reduced volume. Therefore the ratio of the reduced volume of the component to the volume of the entire mixture as expressed in percent will characterize its content in the mixture. For example, in the case worked out above the content of the first component in the mixture comprises 20%, that of the second is 30%, and that of the third is 50%.

One should not consider that these figures correctly reflect the weight ratio between the components. Quite the contrary, if the densities of the components taken at equal temperature and pressure differ from one another the weight ratio between them will be quite different. We will assume that the first component is oxygen and the third is hydrogen. We know that the density of hydrogen is 16 times less than the density of oxygen at equal temperature and pressure. Therefore although the mixture contains 2.5 times more hydrogen than oxygen in terms of volume, with respect to weight the value of oxygen in the mixture will be 6.4 times greater than that of hydrogen.

If the volume content of a component in a gas mixture is known it is easy to determine its partial pressure. To do this the reasoning given above must be carried out in reverse order. Thus, if the volume content of hydrogen in a mixture with a pressure of 10 at comprises 20%, this means that its reduced volume comprises 0.2 of the volume of the total mixture and its partial pressure will equal $10 \times 0.2 = 2$ at. It is known that the composition of air includes 21% oxygen and 79% nitrogen,

by volume. This means that if the absolute pressure of the air equals 1 at the partial pressure of the oxygen in it will equal 0.21 and that of the nitrogen will be 0.79 at.

The connection between the partial pressure of a component, p_k , and its volume fraction in the mixture r_k , in % is expressed by the equality

$$p_k = r_k p_{cm} \quad (8)$$

where p_{cm} is the pressure of the mixture.

A correct knowledge of the properties of gas mixtures and, in particular, their volume composition is not entirely necessary for all who are dealing with gaseous fuels, since (as will be shown below) all gaseous fuel represents nothing more than mechanical mixtures of different combustible and incombustible gases.

Transport Phenomenon

The chaotic motion of gas molecules determines the property of neighboring layers of a gas flow to resist mutual displacement. The force of this resistance is called internal friction or the *viscosity* of the gas.

If in a gas flow its individual layers move parallel to one another, sliding along relative to one another, an exchange of energy will occur on the imaginary surface separating two imaginary layers because of the fact that a certain part of the molecules of the layer moving with great velocity will transfer into a layer moving at a lower velocity, thus accelerating its motion; on the other hand, part of the molecules from the second layer will transfer into the first and will slow its motion.

Thus the viscosity of a gas can be measured as the algebraic sum of the moments (which are the products of mass times the velocity) which are exchanged by layers of gas per unit time. When related to a unit of the surface separating the considered layers this force represents the tangential stress of the boundary surface. As indicated by the law of viscosity established by Newton, tangential stress of a boundary surface is directly proportional to the change in the velocity of gas flow per unit length in a direction perpendicular to this surface (i.e., the flow velocity gradient). This proportionality is characterized by the *coefficient of dynamic viscosity*: the greater the magnitude of the latter, the higher the resistance which mutually displacing layers of gas exert on each other.

A characteristic feature of gases is the fact that with an increase in temperature the viscosity of gases grows. This is explained by the fact that with an increase in temperature the intensity of thermal (chaotic) motion of molecules grows and, consequently, the mutual exchange of moments is accelerated. It is pertinent here to point out that in fluids viscosity is reduced with an increase in temperature. The viscosity of gases is the first of the so-called transport phenomena which represent the consequences of the chaotic motion of gas molecules.

The second of these is molecular diffusion, whose essence is as follows. If for any reason the concentration of an immobile gas turns out to be different on different segments of the volume occupied by this gas, chaotic motion of molecules causes spontaneous leveling of the concentration. Nonuniform concentration of a gas is observed most frequently when two different gases are mixed. In this case there is spontaneous mutual penetration of the gases, completing the formation of a mixture with uniform distributions of both gases in it. This is the phenomenon which is called molecular diffusion. Molecular diffusion is examined in more detail in Chapter V.

Finally the third transport phenomena is called the *heat conductivity* of gases; its essence is as follows. If for any reason the distribution of temperature in a volume occupied by an immobile gas is nonuniform, the chaotic motion of molecules and the exchange of energy between them during collision will lead to spontaneous leveling of the temperature. This property of gases is called thermal conductivity. As shown by the *law of thermal conductivity* established by Fourier, the heat flow from a more heated region to a less heated region of a gas, i.e., the quantity of heat passing per unit time through a unit of the imaginary boundary surface, is directly proportional to the temperature gradient.

This proportionality is characterized by the *coefficient of thermal conductivity*; the greater the value of the latter, the greater the heat flow at one and the same temperature gradient. Naturally, the coefficient of thermal conductivity of a gas is increased with an increase in temperature, when the intensity of thermal motion of molecules grows.

As the material outlined above indicates, the phenomena of viscosity, molecular diffusion, and thermal conductivity have one and the same mechanism, caused by the chaotic motion of molecules. In the first case there is transfer of momentum by molecules, in the second case transfer of the molecules themselves, and finally in the third case transfer of thermal energy by the molecules. It is characteristic that in all three cases the process is directed toward spontaneous leveling of the transferred object in the volume in which the process occurs.

Properties of Real Gases

As was already indicated, all gases which actually exists differ from ideal gases to one or another degree with respect to properties; this is explained by the presence of a certain finite

volume of the molecules (owing to this a part of the gas volume is occupied by the molecules themselves) and by the action of intermolecular forces. For one and the same gas this deviation is the greater the lower the temperature and the higher the pressure. Besides this, through a change in temperature and pressure all real gases can be converted into liquids. There is a qualitative conversion of the physical state connected with a radical change in all of its physical properties. The most substantial of these is the fact that with conversion of a gaseous body into a liquid state it becomes incompressible, while a characteristic feature of gases is precisely their compressibility.

However, for each gas there exists a certain temperature above which it cannot be converted to the liquid state, no matter how high the pressure is raised. This temperature is called the *critical temperature*, and the pressure required for compression liquification of the gas at this temperature is called the *critical pressure*. In the same way, the specific volume of a gas at critical pressure and temperature is called the *critical specific volume*.

Some real gases are in a state of saturation, i.e., in the state of the beginning of condensation (conversion to a liquid) even at parameters which are close to normal. Among the gases which may be found in gaseous fuel these include propane, butane, propylene, and butylene. A gas which with a given pressure (or partial pressure if it is included in the composition of a gas mixture) has a saturation temperature is said to be saturated with vapor. If its temperature is somewhat higher than the saturation temperature it is called superheated vapor [steam]. The boundary between the gaseous and vapor states is considered to be the critical temperature.

The pressure at which vapors with a given temperature are in the saturated state is called the *tension* of the given saturated

vapor. By comparing the pressure of the vapor at a given temperature with its tension in the saturation state it is possible to visualize just how close the state of the given vapor is to saturation - i.e., to what extent its properties differ from the properties of an ideal gas. An equally graphic picture of the degree of deviation of a real gas from the properties of ideal gases is provided by its saturation temperature at normal pressure.

Components of Gaseous Fuel

As is clear from the content of Chapter I, all gaseous fuel represents mixtures of various gases, both combustible and incombustible. The incombustible portion, called the ballast, may contain carbon dioxide, nitrogen, and oxygen. All other [ballast] components are harmful impurities which must be removed from gaseous fuel before it is used. The basic physical characteristics of the enumerated components of gaseous fuel are given in the table. To supplement the data in this table we will examine each of these components individually.

Hydrogen H_2 is the lightest gas occurring in nature; it is colorless and odorless. It has no toxic properties, i.e., it does not have a poisonous effect on the organism of humans or animals. At a substantial content in the air hydrogen will cause suffocation; this is connected with the corresponding reduction in the oxygen content.

Carbon monoxide CO is a product of incomplete combustion of carbon. It is colorless and odorless. CO is strongly toxic; a quantity of 0.025 vol. % in indoor air will cause mild poisoning, while a quantity of 1% will lead to death within 1-2 minutes. Thus, even a brief period of time spent in an atmosphere poisoned by CO is extremely dangerous.

Hydrogen and carbon monoxide are components which are typical of gaseous fuels obtained artificially. They are not found in gases of natural origin.

Methane CH_4 is the lightest of the hydrocarbons (chemical compounds of carbon with hydrogen) and is a colorless, odorless gas. Like hydrogen, it is not toxic but in a large concentration in air will cause suffocation. Methane is the basic component of all natural gas; it is also found in the majority of synthetic gases.

Heavy hydrocarbons - the collective name for all hydrocarbons with no less than two carbon atoms in the molecule. The chemical formula for heavy hydrocarbons in general form is written as C_nH_m . A distinction is made between saturated hydrocarbons, in which the molecule is completely saturated by hydrogen atoms, and unsaturated hydrocarbons, for which the number of [H] atoms in the molecule is less than that in saturated hydrocarbons containing exactly the same number of carbon atoms.

The *saturated* heavy hydrocarbons include all homologs of methane: hydrocarbons characterized by the general formula $\text{C}_n\text{H}_{2n+2}$ which together with methane form a single homolog series (paraffinic hydrocarbons or alkanes). Those of them which are in the gaseous state at their partial pressure and a given temperature of the fuel can enter into the composition of the gaseous fuel. The principle compounds are ethane, propane and butane. All of these gases are colorless and have no odor. Their physical properties are directly connected with molecular weight: the higher the latter, the more they deviate from the properties of ideal gases. The toxic properties of saturated hydrocarbons are also connected with molecular weight, increasing as it increases.

Basic physical characteristics of certain gases.

(1) Имя газа	(2) Химическая формула	(3) Молекулярный вес μ	(4) Плотность при нормальных условиях ρ_0 , кг/м ³	(5) Плотность по воздуху δ	(6) Температура кипения при нормальном давлении t_k , °C	(7) Критические параметры		
						температура $t_{кр}$, °C	давление $p_{кр}$, атм	плотность $\rho_{кр}$, кг/м ³
(11) Водород	H ₂	2,016	0,0898	0,070	-253	-239,0	13,2	31
(12) Окись углерода	CO	28,01	1,250	0,967	-190	-140,2	35,6	301
(13) Метан	CH ₄	16,04	0,717	0,554	-161	-82,1	45,8	162
(14) Этан	C ₂ H ₆	30,05	1,344	1,038	-84	32,3	48,2	203
(15) Пропан	C ₃ H ₈	44,06	1,967	1,523	-44	95,7	43,4	226
(16) n-Бутан	C ₄ H ₁₀	58,08	2,538	2,007	-0,5	152,8	35,7	225
(17) Изобутан	C ₄ H ₁₀	58,08	2,534	2,007	-10	134,0	36,1	214
(18) Пентан	C ₅ H ₁₂	72,05	3,250	2,618	-104	0,8	52,7	210
(19) Гексан	C ₆ H ₁₄	86,08	4,080	3,253	-97	91,0	47,0	233
(20) Гептан	C ₇ H ₁₆	100,10	4,910	3,937	-5	47,2	40,0	—
(21) Изокислот углерода	CO ₂	44,01	1,977	1,520	-78	31,1	75,3	468
(22) Азот	N ₂	28,02	1,251	0,967	-185	-147,1	34,9	311
(23) Кислород	O ₂	32,00	1,429	1,105	-183	-118,4	51,7	411
(24) Водяной пар	H ₂ O	18,02	0,805	0,623	100	374,1	225,6	324
(25) Сухой воздух	—	28,95	1,293	1,000	-191	-140,7	38,4	310

KEY: (1) Name of gas; (2) Chemical formula; (3) Molecular weight, μ ;
 (4) Density in normal conditions, ρ_0 , kg/m³; (5) Density in terms of air, δ ;
 (6) Boiling temperature at normal pressure t_k , °C; (7) Critical parameters;
 (8) temperature $t_{кр}$, °C; (9) pressure $p_{кр}$, атм; (10) density $\rho_{кр}$, kg/m³;
 (11) Hydrogen; (12) Carbon monoxide; (13) Methane; (14) Ethane; (15) Propane;
 (16) n-butane; (17) Isobutane; (18) Ethylene; (19) Propylene; (20) Butylene;
 (21) Carbon dioxide; (22) Nitrogen; (23) Oxygen; (24) Water vapor; (25) Dry air.

Ethane C_2H_6 is close to air in density and under normal conditions can be regarded as an ideal gas.

Propane C_3H_8 - this is a heavy gas whose density equals the density of carbon dioxide. Under ordinary normal conditions it is usually close to the beginning of condensation; at normal pressure propane converts to the liquid state at $-44^{\circ}C$, while this conversion requires an absolute pressure of 8.5 at $20^{\circ}C$.

Butane C_4H_{10} - a gas with two isomers, i.e., varieties with identical chemical formulas and, consequently, identical molecular weight but which differ in the arrangement of atoms in the molecule. These are *n*-butane and isobutane. Both isomers easily convert to the liquid state of normal pressure; the respective temperatures are $-0.5^{\circ}C$ and $-10.5^{\circ}C$. At room temperature ($20^{\circ}C$) conversion to the liquid state requires pressures of 2.1 and 3.2 at, respectively.

Ethane, propane, and butane are usually included in the same gaseous fuel as methane but in substantially smaller amounts. In this connection the partial pressures of these gases, and especially those of propane and butane, are very small. Within the composition of a fuel they can be regarded as ideal gases. Propane and butane are the basic components of "liquifying gases," whose properties will be examined below in greater detail.

Under normal conditions the heavier saturated hydrocarbons, beginning with pentane C_5H_{12} , are liquid. Only a small quantity of their vapors can be contained in a gaseous fuel.

The *unsaturated* heavy hydrocarbons which may enter into the composition of gas fuel include ethylene C_2H_4 and its very close homologs - propylene C_3H_6 and butylene C_4H_8 (butylene has three isomers; butylene-1, butylene-2, and isobutylene). The general formula for hydrocarbons of the ethylene homolog series (olefinic hydrocarbons, or alkenes) is C_nH_{2n} . In terms of their physical

properties they are close to the corresponding saturated hydrocarbons. They are found in fairly large quantities in gases obtained during the refining of petroleum products and petroleum. It should be kept in mind that olefines are valuable technological raw materials and therefore they are usually removed from combustible gas before it is used as a fuel.

Carbon dioxide CO_2 is the product of complete combustion of carbon or of carbon monoxide. It is inert - i.e., incapable of combustion. It is colorless and odorless. At normal pressure it converts directly to the solid state, bypassing the liquid phase, at -78°C . This gas is not toxic but when present in sufficient quantities in air (on the order of 5-10%) it will cause suffocation.

Nitrogen N_2 - the basic component of atmospheric air, in which it is present in a quantity of 78.03 vol.%; together with the monatomic "noble" gases present in the air (mainly argon with traces of helium, neon, krypton, etc.) and also with traces of carbon dioxide it makes up 79.01 vol. % of the atmosphere. Although nitrogen is capable of forming compounds with oxygen (nitrogen oxides), this requires special conditions. Nitrogen oxides are formed in a negligible quantity in the process of technical liquifaction of fuel; therefore in heat engineering nitrogen is regarded as an inert gas, incapable of combustion.

Oxygen O_2 - the second largest component of atmospheric air, amounting to 20.99 vol. %. During combustion oxygen plays the role of oxidizer, being used in this way in the overwhelming majority of cases of combustion of fuel. From considerations of explosion safety and protection of gas equipment from corrosion the content of oxygen in gaseous fuel is not allowed to rise above 1%.

Harmful Impurities in Gaseous Fuels and Their Properties

The harmful impurities in gas fuel are divided into chemically active substances which have a corrosive effect on the metals of gas lines and equipment, and materials which are chemically inactive but capable of forming plugs and blocking gas lines. The first materials include hydrogen sulfide, ammonia, hydrogen cyanide, and carbon disulfide; the second group includes tar, dust, naphthalene, and water vapor. Hydrogen sulfide is the only chemically active impurity found in the composition of natural gases; all the others are characteristic only for synthetic gaseous fuels. The last fact relates also to tar and naphthalene.

Hydrogen sulfide H_2S - a colorless gas with a sharp odor of rotten eggs; it is found in the majority of synthetic gases and in some uncleaned natural fuel gases. Because hydrogen sulfide strongly corrodes metals, especially in the presence of moisture, and because during combustion it yields the gas SO_2 which is no less severe a problem from the point of view of corrosion, its content in gaseous fuel may not exceed 2 g per 100 m^3 of gas after cleaning of the latter.

Ammonia NH_3 - a colorless gas with the odor of ammonium hydroxide, usually found in synthetic gases obtained from solid fuel by destructive distillation. This gas causes corrosion of bronze parts of gas-line equipment and therefore content in gaseous fuel may not exceed 2 g per 100 m^3 of gas.

Hydrogen cyanide HCN - a highly volatile fluid which appears as a result of reacting ammonia with incandescent coke in the process of destructive distillation of solid fuel. Its vapors corrode metal and therefore the content of hydrogen cyanide, along with all other cyanide compounds, cannot exceed 5 g per 100 m^3 in a gaseous fuel.

Carbon disulfide CS_2 - also a highly volatile liquid which can be found in gaseous fuel obtained by destructive distillation of coal and rendering a corrosive effect on the metal of gas lines and equipment.

All of the chemically active impurities listed above are extremely toxic and the content of them in the air of production areas, like that of carbon monoxide, is strictly controlled by appropriate industrial hygiene standards. Thus, the maximum permissible concentration of CO in the air of a working area is 0.03 mg/l; that of hydrogen sulfide is 0.01, for ammonia 0.02, for hydrogen cyanide 0.0003, and for carbon disulfide 0.01 mg/l.

The chemically inactive substances - tar, dust, and especially naphthalenes - can form accumulations and plugs in gas lines (at corners, in junctions of tubes with different diameters, at tee-joints, X-joints, pipe connection points, and points at which equipment is installed). In this connection the content of tar and dust cannot exceed 0.1 g per 100 m³; the norm for naphthalene is 5 g/100 m³ in summer and 10 g/100 m³ in winter.

The presence of water vapor in a gas fuel can hamper the normal operation of gas lines to an even greater degree. Being subject to the general laws of physics, this vapor under certain temperature conditions can convert to the liquid and even the solid state (water, ice), forming accumulations and plugs which block off the gas-line cross section. Besides this, at certain temperatures and in the presence of water in the liquid phase hydrocarbon gases saturated with water vapor can form compounds with it which are called crystal hydrates. In external appearance these compounds are white, ice-like crystalline masses. They are chemically unstable and comparatively easily decomposed into their component parts - hydrocarbon and water.

The crystal hydrates of methane ($\text{CH}_4 \cdot 7\text{H}_2\text{O}$), ethane ($\text{C}_2\text{H}_6 \cdot 8\text{H}_2\text{O}$) and propane ($\text{C}_3\text{H}_8 \cdot 18\text{H}_2\text{O}$) have a melting temperature which is higher than the freezing temperature of ordinary water. This is very important because it influences the conditions in which crystal hydrates are formed: they are formed when water is present in the gas line in the liquid phase and when the temperatures of the gas are lower than the melting temperature of the crystal hydrates.

In order to eliminate the possibility of formation of crystal hydrates and also to prevent the appearance of water, ice, or snow plugs in gas lines the gaseous fuel should be dried to such a degree that its relative humidity will be no more than 60% for the lowest possible temperature in the gas line.

Special Features of Liquified Gases

The physical properties of heavy hydrocarbons as possible components of gas fuel were examined briefly above. However, considering the fact that they are frequently used independently as a fuel of the name "liquified gases" their properties should be examined in more detail.

The graph (Fig. 14) shows curves of vapor tension for propane and butane and also for the olefines corresponding to them - propylene and butylene. The graph shows that these hydrocarbons are comparatively easy, by moderate compression, to be converted into the liquid state. This property is used for their transportation in tanks and bottles in liquid form with subsequent combustion in the form of a gaseous fuel. The convenience of utilizing such fuel in regions far removed from systems of main gas lines is unquestionable; under the name "liquified gas" this technique is finding ever wider application.

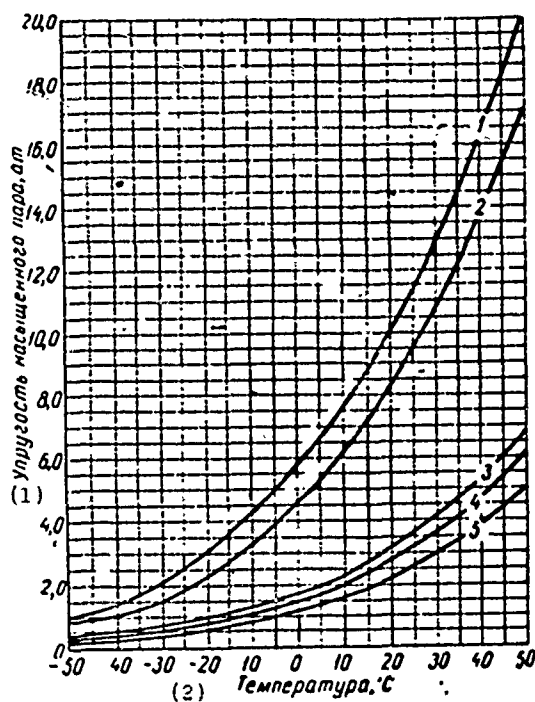


Fig. 14. Curves of hydrocarbon vapor tension. 1 - propylene; 2 - propane; 3 - isobutane; 4 - isobutylene; 5 - *n*-butane. KEY: (1) Saturated vapor tension, at; (2) Temperature, °C.

In the majority of cases liquified gases produced at natural gasoline works are mixtures of propane and butane. The ratio between these components in the mixture is determined by the temperature at which the liquified gas is stored. Mixtures with propane contents up to 30% are used in regions with warmer climates and in the summer months. Mixtures with propane contents no lower than 70% are used in colder regions and in the winter.

Thanks to the similiarity in the molecular structure of propane and butane their liquid mixtures obey Raoult's law, which states that the partial pressure p_H of each component of a liquid mixture equals the molecular concentration of the component in this mixture, x_H , multiplied by its vapor tension Π in pure form at a given temperature, i.e.,

$$p_H = x_H \Pi. \quad (9)$$

Here we must bear in mind that the term molecular concentration of a component is understood to mean the ratio of the number of kilomoles of this component in the mixtures to the total number of kilomoles in the mixture. With phase equilibrium, i.e., when the partial pressures of the component of the vapor and liquid phases are identical, the following equality obtains:

$$r_k p_{cm} = x_k \Pi. \quad (10)$$

where r_k is the volume fraction of the component in the gas phase.

Thus, if the composition of the liquid phase, expressed in molecular concentration of the components, is known it is possible to determine the composition of the vapor phase, expressed in the volume fractions of its components:

$$r_k = x_k \frac{\Pi}{p_{cm}}. \quad (11)$$

Example 4. Required: to determine the saturated vapor tension and volume composition of a mixture in the liquid phase at 20°C, consisting of 70% propane, 20% *n*-butane, and 10% isobutane.

On the graph (see Fig. 14) find the tension of saturated vapors of propane (8.2 at), *n*-butane (2 at), and isobutane (3 at) for 20°C. According to the given example the molar concentrations of components comprise 0.7, 0.2, and 0.1 respectively. According to equations (7) and (8) we can determine the tension of saturated vapors of a mixture of the given composition:

$P_{cm} = 8.2 \cdot 0.7 + 2.0 \cdot 0.2 + 3.0 \cdot 0.1 = 7.04$ at. The volume fractions of the components of the gas phase will be determined from equation (11); for propane $r_1 = 0.7(8.2)/(7.04) = 0.815$; for *n*-butane $r_2 = 0.2(2.0)/(7.04) = 0.057$; and for isobutane $r_3 = 0.1(3.0)/(7.04) = 0.128$.

Liquified gases produced at petroleum refineries always contain a certain quantity of olefinic hydrocarbons - propylene and butylene. Since these differ from the corresponding paraffinic hydrocarbons - propane and butane - in molecular structure, when formulas (9), (10), and (11) are applied to liquified gases of this type they give a certain degree of error.

If vapor is removed from a bottle containing liquified gas, the first to evaporate will be propane, as the lowest-boiling component. As a result, the liquid in the gas bottle will be enriched with the lower-boiling component - butane - as the gas is consumed. There will be a corresponding reduction in the pressure in the bottle.

For example, if a mixture contains 30% propane and 70% butane in the initial state, with a saturated-vapor tension equalling 3.96 at at 20°C, after consumption of 50% its propane content will be reduced to 12% and the butane content will be increased to 88%, with a reduction in saturated-vapor tension to 2.8 at; after 70% of the mixture has been used the propane content equals 5% and the butane content 95%, with a reduction in saturated-vapor tension to 2.37 at.

The considered circumstance indicates that reliable operation of the gas equipment using liquifying gas as a fuel requires that the composition of the gas be determined on the basis of the condition of permissible reduction in pressure. The minimum permissible excess pressure of the gas in the container should be considered 0.35 at at any possible reduction in temperature.

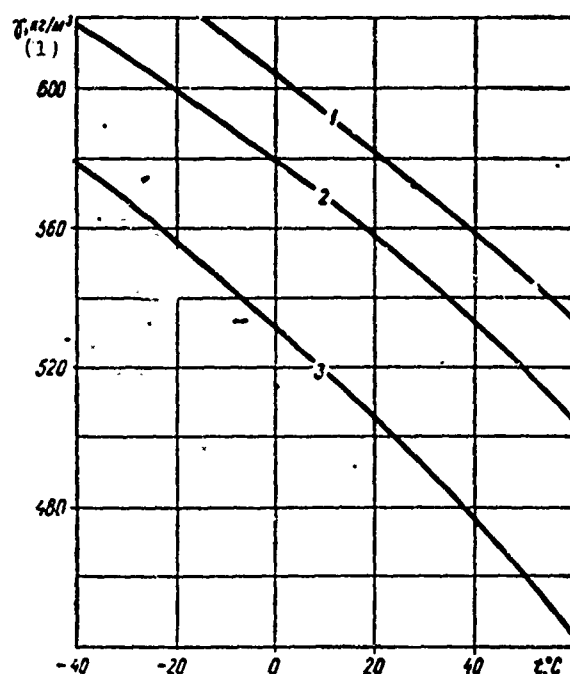


Fig. 15. Specific weight of components of liquified gases as a function of temperature. 1 - n-butane; 2 - isobutane; 3 - propane.
KEY: (1) γ , kg/m³

An extremely essential feature of liquified gases is the low density of the liquid phase (as compared with water) and, the main point, the very high coefficient of volume expansion. These properties are clearly illustrated by the graph (Fig. 15). For example, at 0°C propane has a density of 532 kg/m³ (only 53.2% of the density of water), while at 50°C it is reduced to 462 kg/m³ - i.e., the specific volume grows by 15.4% (from 1.88 to 2.17 l/kg). In this connection the "Safety Rules for the Gas Industry" provide that the level to which reservoirs and bottles are filled should be selected with regard to the density of the liquified gas and the difference in its temperature at the time of filling and during subsequent storage. When the temperature difference falls in the limits of 40 degrees the filling level is taken as 85%, while with a greater temperature difference it should be appropriately reduced.

If the temperature difference Δt is known, the filling factor for a bottle to be filled with the liquid phase is

$$k = \frac{1}{1 + \Delta t \varphi} \quad (12)$$

where φ is the volume expansion factor of the liquid phase.

CHAPTER III

COMBUSTION OF GASEOUS FUEL

Chemical Reactions and the Thermal Effect of Total Combustion of Gases

In the broad sense of the word the combustion of fuel represents the totality of physical and chemical processes which include mixing the fuel with air, heating of the mixture, thermal decomposition of the fuel, ignition, and finally the chemical combination of the fuel with atmospheric oxygen, connected with intensive heat liberation and therefore accompanied by a sharp increase in temperature. In a narrower sense, as the term is used in this section, combustion can be defined as the chemical reaction of combination of the combustible components of a gas fuel with atmospheric oxygen.

Of all the substances which are capable of entering into chemical combination with oxygen the most important is carbon, which constitutes the basic component in virtually all types of industrial fuels - coal, petroleum, natural gas, other forms of gas fuel, fuel shales, wood fuel, etc.

Each atom of carbon which combines with one molecule of oxygen is converted into a single molecule of carbon dioxide: $C_2 + 2O_2 = 2CO_2 + 8100 \text{ Cal.}$ This is what determines the ratio of

weight between carbon, oxygen, and carbon dioxide as they participate in the reaction. In this process heat is obtained due to the fact that the energy included in the atoms of carbon in the form of "latent" chemical energy is liberated and takes the outwardly perceptible form of thermal energy, i.e., kinetic energy (energy of motion) of the molecules of carbon dioxide. Each kilogram of carbon which is completely oxidized with the formation of carbon dioxide yields 8100 Cal. The carbon dioxide which is obtained cannot enter into any further reaction with oxygen - i.e., from the point of view of the combustion process it is an "inert" gas.

If there is a deficiency of oxygen the oxidation of carbon may be incomplete. In this case every 12 kg will consume not 32, but only 16 kg of oxygen; here another end product is obtained - carbon monoxide, CO. Naturally, the heat which is liberated is less during such incomplete combustion than during complete oxidation; each kilogram of carbon oxidized to CO yields only 2770 Cal of heat. The rest of the heat remains chemically bound - i.e., it represents the chemical energy of the carbon monoxide which is formed in such a process.

In pure form carbon is not a gas, but a solid. Therefore it does not enter independently into the composition of gas fuels, but rather in the form of various compounds with hydrogen (i.e., the hydrocarbons studied in the preceding chapter) or in the form of carbon monoxide.

A molecule of carbon monoxide (CO) consists of one atom of carbon and one atom of oxygen; consequently its molecular weight is 28. Since it is the product of incomplete oxidation, carbon monoxide itself is a combustible gas capable of further oxidation. On the basis of molecular weights it is possible to compile the material balance of the process of oxidation of carbon monoxide: oxidation of 28 kg of CO requires 16 kg of oxygen; as a result of

the reaction $28 + 16 = 44$ kg of carbon dioxide will be formed. Calculation on volume units shows that under normal conditions 0.5 m^3 of oxygen will be expended per 1 m^3 of carbon monoxide. In this case 1 m^3 of carbon dioxide is formed with liberation of 3020 Cal.

We will now examine the material balance and heat liberation of the hydrogen oxidation reaction. Water vapor, H_2O is formed with the result of this reaction. In the reaction each molecule of reacting oxygen is attached to two molecules of hydrogen and two molecules of water vapor are formed. Since the molecular weight of hydrogen equals 2, 8 kg of oxygen are expended for each kilogram of H_2 ; as a result $1 + 8 = 9$ kg of water vapor will be formed and 28,800 Cal will be liberated: $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O} + 28,800 \text{ Cal}$. Conversion to volume units shows that under normal conditions 0.5 m^3 of oxygen is consumed per 1 m^3 of hydrogen, with the formation of 1 m^3 of water vapor and the liberation of 2570 Cal.

The last quantity represents the *lowest heat of combustion* of hydrogen; it does not take into account that latent heat which is contained in the water vapor and, actually representing a part of the heat liberated in the course of the reaction, cannot be used without condensation of water vapor combustion products (in the overwhelming majority of cases this does not occur). The *highest heat of combustion* of hydrogen - i.e., all of the chemically bound heat which is liberated during its oxidation - exceeds the lowest value by the magnitude of this latent heat and comprises 3050 Cal/m^3 .

Like carbon dioxide, water vapor is the product of a complete oxidation and therefore from the point of view of the combustion process it is also an inert material, incapable of further oxidation.

A molecule of methane, the basic component of all gaseous fuel of natural origin, consists of one atom of carbon and four

atoms of hydrogen. Consequently its molecular weight comprises $12 + 4 \cdot 1 = 16$. The total oxidation of methane results in the formation of carbon dioxide (one molecule for each molecule of methane) and water vapor (two molecules for each molecule of methane): $\text{CH}_4 + 2\text{O}_2 = \text{CO}_2 + 2\text{H}_2\text{O}$.

On the basis of the molecular weights of the components in the reaction under examination, the complete oxidation of 16 kg of methane will require $2 \cdot 32 = 64$ kg of oxygen, with 44 kg of carbon dioxide and $2(2 + 16) = 36$ kg of water vapor being formed as the result of the reaction. Knowing the ratio between the molar quantities of the reaction components and considering that the moles of these gases occupy identical volumes under identical conditions, we easily convert to volume relationships, finding that: during complete oxidation 2 m^3 of oxygen are consumed per 1 m^3 of methane, with the formation of 1 m^3 carbon dioxide and 2 m^3 of water vapor. Without consideration of the latent heat of the water vapor which is formed, the liberation of heat in this reaction comprises 8560 Cal/m^3 ; this quantity represents the lowest heat of combustion of methane.

By similar reasoning we can compile the material balance of the reaction of total oxidation of any of the heavy hydrocarbons. The lowest heat of combustion in Cal/m^3 for some of the heavy hydrocarbons can be taken from the following data obtained on the basis of experiment:

Ethane C_2H_6	15,370
Propane C_3H_8	22,350
n-Butane C_4H_{10}	29,050
Isobutane C_4H_{10}	29,510
Ethylene C_2H_4	14,320

Propylene C_3H_6 21,070

Butylene C_4H_8 27,120

The heat of combustion of hydrocarbons depends strongly on molecular weight: the heavier the hydrocarbon, the greater its heat of combustion. The given data permit us to determine the heat of combustion for any gaseous fuel which is a mixture of various components if its volume composition is known, since the role of each of the combustible components in the total heat liberation is proportional to its volume fraction:

$$Q_{cm} = r_1 Q_1 + r_2 Q_2 + \dots + r_n Q_n \quad (13)$$

Q_{cm} is the heat of combustion of the mixture, Cal/m³; r_1, r_2, \dots, r_n represent the volume fractions of the combustible components of the mixture; Q_1, Q_2, \dots, Q_n are the heats of combustion of the combustible components of the mixture in Cal/m³.

Example 5. Determine the lowest heat of combustion of a gas characterized by the following volume composition (%): $H_2 = 58$; $CO = 7$; $CH_4 = 26$; $C_2H_6 = 1$; $C_3H_8 = 0.6$; $C_2H_4 = 0.4$; $CO_2 = 2$; $N_2 = 4$; $O_2 = 1$.

$$\text{According to formula (13)} \quad Q_{cm} = \frac{58}{100} \cdot 2570 + \frac{7}{100} \cdot 3020 + \frac{26}{100} \cdot 8560 + \frac{1}{100} \cdot 15370 + \\ + \frac{0.6}{100} \cdot 22350 + \frac{0.4}{100} \cdot 14320 = 1191 + 211 + 2228 + 154 + 134 + 57 = 4275 \text{ Cal/m}^3.$$

The Quantity of Air Required for Complete Combustion of a Gaseous Fuel

For correct organization of the process of burning gas it is necessary to be able to determine the quantity of air required for complete burning of each cubic meter of this gas. This is not difficult to do; we can be convinced of this by studying the following example.

Example 6. Required: to find the quantity of air theoretically required for complete combustion of 1 m^3 of a mixed gas whose volume composition includes 6% H_2 , 2% carbon monoxide, and 90% methane. The remaining 2% is ballast - 1% nitrogen and 1% carbon dioxide. We will begin with determination of the theoretically required quantity of oxygen. Since we know that the combustion of 1 m^3 of hydrogen requires 0.5 m^3 of oxygen, we find that the 0.06 m^3 of hydrogen included in each 1 m^3 of our gas receives 0.03 m^3 of oxygen. In the same way we know that total combustion of 1 m^3 of carbon monoxide requires 0.5 m^3 of oxygen. Consequently 0.01 m^3 of oxygen will be required to burn the 0.02 m^3 of carbon monoxide included in each 1 m^3 of our gas. It is known that the combustion of 1 m^3 of methane requires 2 m^3 of oxygen. Consequently 1.8 m^3 of oxygen must be used to burn the 0.9 m^3 of methane found in each 1 m^3 of our gas. We will now add up all the obtained volumes; we find that complete combustion of 1 m^3 of our mixed gas will theoretically require $0.03 + 0.01 + 1.8 = 1.84 \text{ m}^3$ of oxygen. Air consists of 21% oxygen and 79 vol. % nitrogen. This means that the amount of air required for combustion will be 4.76 times as great as the oxygen requirement. Therefore, by multiplying 1.84 by 4.76 we obtain the figure 8.76 m^3 . This is the quantity of air theoretically necessary for complete combustion of 1 m^3 of our gas.

The calculations given above express in general form the formula which allows determination of the theoretically required quantity of air for any gaseous fuel whose composition is given:

$$V_o = \frac{100}{21} \left[0.5 \frac{\text{H}_2}{100} + 0.5 \frac{\text{CO}}{100} + \sum \left(n + \frac{m}{4} \right) \frac{\text{C}_n\text{H}_m}{100} - \frac{\text{O}_2}{100} \right] [\text{m}^3/\text{m}^3],$$

or, in simpler form,

$$V_o = 0.0238 \text{C}[\text{O} + \text{H}_2 + 2 \sum (n + 0.25m) \text{C}_n\text{H}_m - 2\text{O}_2], \quad (14)$$

where the next to the last term inside the braces relates to combustion of all hydrocarbon gases and represents the sum of the components whose number equals the number of hydrocarbons contained in the fuel.

Thus, if a fuel contains methane, ethane, propane, and butane, then $\sum \left(n + \frac{m}{4}\right) \frac{C_n H_m}{100} = \left(1 + \frac{2}{4}\right) \frac{CH_4}{100} + \left(2 + \frac{6}{4}\right) \frac{C_2 H_6}{100} + \left(3 + \frac{8}{4}\right) \times \frac{C_3 H_8}{100} + \left(4 + \frac{10}{4}\right) \frac{C_4 H_{10}}{100} = 0.01 (2CH_4 + 3.5C_2H_6 + 5C_3H_8 + 6.5C_4H_{10}) [m^3/m^3]$.

In the operation of equipment working on gas it happens most frequently that the composition of the gas is unknown but its heat of combustion is known. The following practical rule has been developed for this case: 1.13 m³ of air will theoretically be required for each 1000 Cal of the lowest heat of combustion of a gaseous fuel consisting mainly of hydrocarbon gases. For example, if the heat of combustion of gas equals 8000 Cal/m³, the theoretically required quantity of air comprises 1.13 · 8 = 9 m³/m³.

As we have shown, determination of the quantity of air theoretically required for combustion of a gas is comparatively simple. However, it is easy to understand that the quantity of air found in actuality may turn out to be inadequate. Actually, for complete combustion of a gas it is necessary that all the molecules of oxygen contained in the theoretically required quantity of air be completely used up. In practice this is impossible. The mixing of the combustible gas with air, accomplished by means of a gas burner, will never be ideal. Always some portion of the oxygen molecules (a larger or smaller amount, depending on the quality of mixing) will fail to contact molecules of the combustible components of the gas and therefore cannot take part in the combustion process.

To guarantee complete combustion air must be fed into the furnace not in the theoretically required amount but in a certain excess, bearing in mind that part of the air remains unusable due to imperfect contact between molecules of oxygen and those of the combustible components of the gas.

Finally, the ratio between the actual and theoretically required quantity of air may differ as a function of the ability of the gas to burn (its ability to mix with air). If the gas is well mixed with all the air required for combustion before it enters the furnace (for example, in medium-pressure injection burners), there is no need to create a large excess of air. In this case only about 5% of the theoretically necessary amount is added. Consequently, the ratio of the entire quantity of air supplied to the furnace to the theoretically required volume comprises 1.05.

If the gas is fed to the furnace separately from air and mixed with it only as a result of the comparatively slow process of diffusion (as occurs in diffusion burners), the achievement of complete combustion requires creation of a large excess of air in the furnace. In such cases the ratio of the total quantity of air supplied to the furnace vs. the theoretically required amount reaches 1.3 and even more — i.e., the quantity of excess air comprises 30% and more of the theoretically required amount. *The ratio of the quantity of air which is actually fed into the furnace and the theoretically required amount is called the excess air ratio, α .* The magnitude of the required excess air coefficient which must be maintained during burning of a gas is established individually for each case and for each type of gas burner.

The Quantity of Products of Complete Combustion of a Gaseous Fuel

We will consider the combustion products formed during the burning of a gas. If combustion is complete the combustion products may consist only of inert gases — i.e., gases which are incapable of further oxidation. Actually, during complete combustion hydrogen is converted into inert water vapor and carbon monoxide into inert carbon dioxide. During complete combustion methane and other hydrocarbons give the one and the other. Thus,

as a result of complete combustion of any gas, however complex in composition, two inert gases are formed - carbon dioxide and water vapor. However, this does not exhaust the components of the gaseous mixture representing the products of combustion or, as they are still called, the stack gases. The air fed into the furnace carries with it a large quantity of nitrogen which does not participate in any way in the combustion process; it is mixed with the carbon dioxide and water vapor and is included in the stack gases with them. The same is true of the ballast components of the gas and of the oxygen supplied with the excess air (it is clear that if the excess air factor comprises, let us say, 1.25 then during complete combustion of a gas only 80% of the oxygen contained in the air arriving in the furnace will be consumed; the remaining 20% is mixed with the combustion products and is a part of the stack gases).

Thus the stack gases which are formed during complete combustion of any gaseous fuel which has been purified from sulfurous compounds consists of four components: carbon dioxide, water vapor, oxygen, and nitrogen. If the gas composition and excess air factor at which the combustion process is conducted are known it is not difficult to determine the total quantity of stack gases formed.

Example 7. We will examine the combustion of the mixed gas for which the quantity of theoretically required air was determined in Example 6. We will assume that combustion is carried out with an excess air factor $\alpha = 1.2$.

We know that during combustion of carbon monoxide and methane carbon dioxide will be formed in the same quantity as taken for these gases. Consequently, during combustion of 0.02 m^3 carbon monoxide and 0.9 m^3 methane in 1 m^3 of our gas, 0.92 m^3 carbon dioxide will be formed. If we add here 0.01 m^3 carbon dioxide

included in the ballast of the gas being burned, the total quantity of carbon dioxide gas comprises $0.93 \text{ m}^3/\text{m}^3$ of the gas being burned.

We also know that water vapor is formed in a quantity of $1 \text{ m}^3/\text{m}^3$ of hydrogen burned and $2 \text{ m}^3/\text{m}^3$ of methane. Consequently, when 0.6 m^3 of hydrogen and 0.9 m^3 of methane included in 1 m^3 of the gas are burned, $0.6 + 2 \times 0.9 = 2.4 \text{ m}^3$ of water vapor will be formed. To this we must add the water vapor which is always found in the air used for combustion. However, this is a very small amount and it can be completely ignored. Thus, the total quantity of water vapor in the stack gases comprises $2.4 \text{ m}^3/\text{m}^3$ of gas being burned.

The theoretically required quantity of oxygen comprised $1.84 \text{ m}^3/\text{m}^3$ of fuel gas in the preceding example. We know that combustion is carried out with $\alpha = 1.2$. Consequently, the quantity of excess oxygen comprises 20% of the theoretically required amount - i.e., $0.2 \cdot 1.84 = 0.37 \text{ m}^3$. This is the quantity of oxygen which enters into the stack gases formed during combustion of 1 m^3 of gas.

Finally, we know that the combustion products will include all of the nitrogen in the air used and also the nitrogen included in the ballast portion of the combustible gas. Since the volume content of nitrogen in air is 79% and the total quantity of air consumed on combustion per 1 m^3 of gas equals $1.2 \cdot 8.76 = 10.5 \text{ m}^3$, this air will contain $0.79 \cdot 10.5 = 8.29 \text{ m}^3$ of nitrogen. By adding to this the 0.01 m^3 of nitrogen contained in the gas itself we find that the total quantity of nitrogen in the stack gases is $8.3 \text{ m}^3/\text{m}^3$ of the combustible gas.

If we now add the amounts of all components in the stack gases we find the total quantity of stack gases formed during complete combustion of 1 m^3 of the gas: $0.93 + 2.4 + 0.37 + 8.3 = 12.0 \text{ m}^3$.

In essence this is how simple it is to calculate the process of total combustion of any gas, however complex its composition. The single simplification which we allowed in our considerations in order not to burden the reader with excessive calculations was the fact that heavy hydrocarbons were not introduced into the gas composition. However, by using the simple examples outlined above the reader can, if necessary, independently consider their presence in the composition of [any] gas with which he may have to deal.

Generalization of the calculations shown in Example 7 to determination of the quantity of combustion products for a gaseous fuel leads to formulas which should be used in those cases when combustion is assumed to be complete and also when the composition of the fuel and the excess air factor α with which combustion proceeds are known:

quantity of carbon dioxide, m^3/m^3 ,

$$V_{\text{CO}_2} = \frac{\text{CO}}{100} + \sum n \frac{C_n H_m}{100} + \frac{\text{CO}_2}{100} = 0.01 \left(\text{CO} + \sum n C_n H_m + \text{CO}_2 \right); \quad (15)$$

quantity of water vapor (considering the fact that 1 kg of air partaking in combustion contains 10 g of water vapor), m^3/m^3 ,

$$\begin{aligned} V_{\text{H}_2\text{O}} &= \frac{\text{H}_2}{100} + \sum \frac{m}{2} \cdot \frac{C_n H_m}{100} + 0.016 \alpha V_0 = \\ &= 0.01 \left(\text{H}_2 + \sum 0.5 m C_n H_m + 1.6 \alpha V_0 \right); \end{aligned} \quad (16)$$

quantity of oxygen, m^3/m^3 ,

$$V_{\text{O}_2} = 0.21 (\alpha - 1) V_0; \quad (17)$$

quantity of nitrogen, m^3/m^3 ,

$$V_{\text{N}_2} = 0.79 \alpha V_0 + \frac{\text{N}_2}{100} = 0.79 \alpha V_0 + 0.01 \text{N}_2. \quad (18)$$

The Combustion Temperature of a Gas

A mandatory condition for organizing stable and complete combustion of a gas is maintaining a sufficiently high temperature in the furnace. We will consider the factors on which the possibility of fulfilling this condition depends.

During the combustion of a gas the chemical energy which is contained in bound form in the molecules of the combustible components of a gas is liberated and takes the different and visible form of the kinetic energy of the molecules of the combustion products. In other words, during the combustion of a gas its chemical energy is converted into heat and transferred to the combustion products.

A measure of the intensity of the random motion of molecules of a gas which characterizes the heat reserve in this gas is its temperature. Therefore the temperature of the combustion products is found to be very high and, other conditions being equal, this value is the greater the smaller the quantity of gases formed and the less the heat which is given out in the combustion process to the relatively cool surfaces surrounding the furnace.

It is clear that for every gas there exists a maximum temperature of the combustion products. In practice this temperature is unattainable, since obtaining it requires meeting of ideal conditions. These conditions are as follows: combustion must be complete with the minimum possible (i.e., theoretically required) quantity of air and the combustion products must be completely isolated from the environment in terms of heat - i.e., all of the heat liberated during combustion must be consumed only in heating the combustion products. Nonetheless this maximum temperature is an important characteristic of a combustible gas, since it reflects the capability of the gas to maintain the required temperature

level for the combustion process. It is called the *theoretical temperature of combustion*.

By using a basic law of nature — the law of conservation of energy — it is easy to clarify the factors on which the theoretical combustion temperature depends. However, we will first become acquainted with the concept of volumetric heat capacity of gases; this concept is necessary for consideration of various questions of gas technology. *The volumetric specific heat of a gas is that quantity of heat which must be expended to raise the temperature of 1 m³ of this gas by 1°C.* In this case we consider that heating occurs at constant pressure — i.e., under precisely those conditions which are observed in the process of combustion of a gas.

From this definition it is clear that we will obtain the theoretical temperature of combustion if we break down the total heat of the combustion products first into the total quantity of combustion products (to find out how much heat is connected with each cubic meter of combustion products) and secondly into their volumetric specific heat.

Just what amount of heat do the combustion products obtain? Since the theoretical combustion temperature is counted from 0°C, we will consider that the temperature of both the gas and the air before combustion equals 0°C. Then it is obvious that all the heat obtained by the products of combustion of 1 m³ of gas will exactly equal the heat of combustion of this gas. This follows directly from the law of conservation of energy. Thus the theoretical combustion temperature of the gas is the greater the higher its heat of combustion, and it will be the lower the greater the quantity of combustion products formed during burning of 1 m³ of this gas. However, on the other hand it is known that the higher the heat of combustion of gas the greater will be the theoretically required quantity of air; in its turn, this is a

strong governing factor over the quantity of combustion products, since the basis of their composition is the nitrogen obtained from the air. Actually, in the example considered above nitrogen amounted to 8.3 m^3 out of the total quantity of combustion products of 10.5 m^3 . This means that the quantity of combustion products for the gas grows in approximate proportion to its heat of combustion and, consequently, the theoretical combustion temperature is virtually unchanged.

Actually, if we take combustible gases of very different compositions and very different heats of combustion we find that the theoretical combustion temperature differs very little among them. This is especially noticeable in various natural gases or gases which are similar to them in composition. Approximately one and the same value for the theoretical combustion temperature is obtained for all of these gases; it can be considered equal to 2000°C for all of them.

The real combustion temperature is always less than the theoretical (even during complete combustion of the gas) for the following two reasons. First of all, the combustion process always proceeds with an excess of air, which causes growth in the quantity of combustion products (as compared with the theoretical quantity) but with one and the same quantity of heat liberated during combustion of the gas; thus in this case the heat is distributed to a larger quantity of combustion products. Thus, when double the theoretically required quantity of air is supplied the combustion temperature of natural gas (under the condition of complete isolation of the combustion products from the environment) will comprise not 2000°C , but only 1170°C . Secondly, in actual conditions of gas combustion the liberation of heat is accompanied by a loss of part of it to the relatively cold surfaces surrounding the heater. Thus, the combustion products do not receive all of the heat liberated in the combustion process, but only a part of

it. Naturally, this reduces their temperature and consequently the total temperature level of the combustion process is also reduced. Sometimes this reduction is so great that combustion becomes unstable and there is a high degree of incomplete combustion. In such cases it is necessary that the combustion zone be artificially protected from the cooling influence of the heater surfaces. The real temperature of a furnace space, for example, in a steam boiler during combustion of gas is no more than 1100-1200°C.. When the boiler has an air preheater this temperature can, of course, be increased, since the physical heat of the air supplied to the furnace from the preheater is added to the heat of combustion of the fuel.

Thermal Losses During Burning of Gaseous Fuel

We will use the example of operation of the most typical gas-fuel consumer - steam boilers - to examine questions connected with thermal losses during burning of fuel of this type.

Combustible gases and especially natural gas are, in every respect, excellent fuels. When used to heat steam boilers they have many advantages over all other types of fuel. However, for completely effective use of these advantages and to achieve good results in operating a boiler installation on gas it is necessary that a number of special conditions be fulfilled. We speak here not of specific requirements of industrial safety whose total observance is mandatory during operations with gas. These questions have such tremendous significance that they must be the subject of the content of a separate book. We have in mind conditions which ensure economy of operation of a boiler installation - i.e., the rational utilization of combustible gas.

Unfortunately, not all of the chemical energy of a gas can be used profitably when it is burned under steam boilers. Even

modern high-capacity boiler unit, almost all of heat, although every possible measure is taken to ensure economy of operation. This is true to a lesser degree with regard to small steam boilers installed in industrial or heating plants and converted to gas from other types of fuel.

Before we consider the measures directed toward increasing the economy of a boiler installation it is necessary to know the specific types of thermal losses of a steam boiler and their causes.

A part of the heat which is liberated during combustion of a gas is imparted to the radiation heating surfaces surrounding the furnace space (furnace screens) through radiation by incandescent furnace gases. Then passing along the gas ducts of the boiler these gases wash convective heating surfaces arranged in their path (boiler tubes, steam heater, feed-water economizer, air heater). Their temperature is gradually reduced so that strongly cooled gases called stack gases are passed into the chimney. The physical heat of these gases comprises the basic loss of a steam boiler — *loss of heat with stack gases*. It is impossible to eliminate this loss completely, since this would require cooling of the stack gases to the initial temperature of the fuel and draft air; this cannot be accomplished for the simple reason that cooling of the gases in the presence of heating surfaces which are realistic in size would require a very great temperature drop between the gases and the material to be heated (water or air). In the best cases, with the most highly developed boiler unit construction, gases are cooled to 120-140°C. In other cases the temperature of the stack gases may be reduced only to 180-200°C; the temperature may sometimes be even higher. Not all of the physical heat which is carried off by the stack gases represents losses, since a part of it was obtained not during combustion of the fuel but as a "gift" in the form of the physical heat of the air entering the boiler unit.

The physical heat of the stack gases as related to 1 m³ of the gaseous fuel being burned is the product of the quantity of these gases (this determination was described above) times their volumetric specific heat and their temperature. The physical heat of the air arriving in the boiler unit is, in the same way, the product of the quantity of air arriving in the unit times its volumetric specific heat, temperature, and the excess air factor in the stack gases.

The heat loss with stack gases, Q_2 , is the difference between the physical heat of the stack gases and that of the air arriving in the boiler unit:

$$Q_2 = V_{y,r} c_{y,r} t_{y,r} - \alpha_{y,r} V_0 c_a t_a \quad [\text{Cal/m}^3], \quad (19)$$

where $V_{y,r}$ is the total quantity of stack gases, m³/m³; $c_{y,r}$ is the volumetric specific heat of the stack gases, Cal/m³ deg; $t_{y,r}$ is the temperature of the stack gases in °C; $\alpha_{y,r}$ is the coefficient of excess air in the stack gases; V_0 is the theoretically required quantity of air, m³/m³; c_a is the volumetric specific heat of air, Cal/m³ deg; t_a is the temperature of the air, °C.

The relative loss with stack gases expressed in percentage of the lowest heat of combustion of the fuel will be

$$q_2 = \frac{Q_2}{Q_H} \cdot 100. \quad (20)$$

where Q_H is the lowest heat of combustion of the fuel.

Example 8. We will turn to the data in Example 7. We must consider that owing to the imperfect sealing of the steam boiler by the lining and to the presence of rarefaction over the entire path of the stack gases, air from the environment is sucked into them. In the end the excess air factor in stack gases is gradually

increased and is greater when the stack gases leave the boiler unit than it is in the furnace. We will consider that during passage of the stack gases through the gas ducts the excess air factor α is increased from 1.2 to 1.6. Then if the theoretically required quantity of air comprises $8.76 \text{ m}^3/\text{m}^3$ (according to Example 7), the quantity $0.4 \cdot 8.76 = 2.09 \text{ m}^3/\text{m}^3$ will be sucked into the stack gases in the gas ducts of the boiler unit. Now the quantity of stack gases will comprise not $12.0 \text{ m}^3/\text{m}^3$, but $12.0 + 2.09 = 14.09 \text{ m}^3/\text{m}^3$.

The volumetric specific heat of the stack gases can be determined from special tables with consideration of the composition and temperature of the gases. In this case

$$V_{y,r} c_{y,r} = V_{\text{CO}_2} c_{\text{CO}_2} + V_{\text{H}_2\text{O}} c_{\text{H}_2\text{O}} + V_{\text{O}_2} c_{\text{O}_2} + V_{\text{N}_2} c_{\text{N}_2} \quad (21)$$

for values c of specific heat are taken from tables for a given temperature $t_{y,r}$, while the values of the volumes V are found from formulas (15), (16), (17), and (18).

This determination is somewhat laborious; for simplification of this example we will take $c_{y,r}$ as being the same as that for moist air. The error introduced by this simplification is not great. We will assume that the temperature of the stack gases is $t_{y,r} = 200^\circ\text{C}$. According to the table their specific heat comprises $0.318 \text{ Cal}/\text{m}^3 \cdot \text{deg}$. The physical heat of the stack gases will equal $14.09 \cdot 0.318 \cdot 200 = 897 \text{ Cal}/\text{m}^3$.

The total quantity of air arriving in the boiler is $14.0 \text{ m}^3/\text{m}^3$. The air temperature in the boiler is 30°C . From the table its specific heat is $0.315 \text{ Cal}/\text{m}^3 \times \text{deg}$. The physical heat of this air equals $14.0 \cdot 0.315 \cdot 30 = 132 \text{ Cal}/\text{m}^3$. Therefore $Q_2 = 897 - 132 = 765 \text{ Cal}/\text{m}^3$. The heat of combustion of the fuel in our example is $8000 \text{ Cal}/\text{m}^3$. Therefore according to formula (20), $\eta_2 = \frac{765}{8000} \cdot 100 = 9.6\%$.

From Example 8 it is clear that the losses with the stack gases will be the greater, the higher the temperature of the stack gases and the greater their quantity. This means that the maximum possible reduction in heat losses with stack gases requires the following: carry out the combustion process with the lowest permissible excess air factor; provide the best possible sealing by the boiler lining; cool the stack gases to the greatest degree possible by regular removal of deposited soot from the heating surfaces.

If the process of combustion of the gas is incorrectly organized - inadequately perfected mixing with air or too low a temperature in the combustion zone - another heat loss will occur; this is called *losses due to incomplete chemical burning*. Its essence is as follows: combustion is incomplete and the combustion products contain combustible components, primarily hydrogen, carbon monoxide, and sometimes methane and even heavier hydrocarbons. All of these substances are capable of releasing heat during combustion and consequently their presence in the stack gases indicates that a part of the chemical energy of the fuel was not liberated during combustion and is lost during escape of the stack gases from the boiler unit.

Heat losses due to incomplete chemical burning, Q_3 , can be determined from a formula which takes into account the possible presence of hydrogen, carbon monoxide, and methane in the stack gases:

$$Q_3 = \left(2570 \frac{H_2}{100} + 3020 \frac{CO}{100} + 8560 \frac{CH_4}{100} \right) V_{c.y.r} [m^3/m^3], \quad (22)$$

where H_2 , CO , CH_4 are the percentage contents of hydrogen, carbon monoxide, and methane in dry stack gases; $V_{c.y.r}$ is the quantity of dry stack gases related to 1 m³ of fuel burned.

Relative losses due to incomplete burning, expressed as a percentage of the lowest heat of combustion of the fuel, will be

$$q_3 = \frac{Q_3}{Q_u} \cdot 100. \quad (23)$$

Example 9. Using data from Examples 7 and 8, determine q_3 . Consider that as a result of an incomplete combustion process the dry portion of the stack gases contains 0.8% hydrogen and 0.5 vol. % carbon monoxide.

It was established earlier that the total quantity of combustion products with $\alpha = 1.6$ will comprise $14.09 \text{ m}^3/\text{m}^3$. In this case the fraction of water vapor was 2.4 m^3 . Consequently, the quantity of dry combustion products $V_{c.y.r} = 14.09 - 2.4 = 11.69 \text{ m}^3/\text{m}^3$.

$$Q_3 = \left(2570 \frac{0.8}{100} + 3020 \frac{0.5}{100} + 8560 \frac{0}{100} \right) \cdot 11.69 = 412 \text{ Cal}/\text{m}^3.$$

The relative losses due to incomplete chemical burning will be $q_3 = \frac{412}{8000} \cdot 100 = 5.1\%$.

This example shows that the presence of combustible components in the stack gases, even if they amount only to a fraction of a percent, will cause a very great loss due to chemically incomplete burning. Therefore the burning of a gas should be organized in such a way that there will be no combustible components in the stack gases.

During operation of a steam boiler the temperature of its walls is much higher than that of the surrounding air. This air is heated, picking up heat from the boiler unit and causing a third loss of heat, called *losses to the environment*.

The magnitude of these losses, Q_3 , [sic] depends mainly on the difference in temperatures between the outer surface of the

lining and the surrounding air; it also depends on the area of the surface. Therefore the relative loss of heat to the environment

$$q_5 = \frac{Q_5}{Q_n} \cdot 100 \quad (24)$$

depends on the quantity of gas burned — i.e., on the boiler load — and is reduced with an increase in the latter. This explains to a substantial degree the fact that the boiler will operate more economically at heavy loads than at small loads. The relative magnitude of the outer surface of the lining in small boilers is greater than that for large boilers. Therefore heat losses to the environment by high-capacity boilers with a steam productivity of several hundred tons of steam per hour represent a quantity of the order of 0.5% (at rated loads); in small boilers it is substantially greater, reaching up to 4-6%. Determination of q_5 is a very complex problem and therefore this quantity is usually given with respect to existing norms.

If the total heat losses discussed above are subtracted from the total quantity of heat which can be obtained during burning of a gas, the quantity left represents the amount of useful heat which is expended directly on the development of steam. If we express the useful heat in percentages of the lowest heat of combustion, we will obtain the most important characteristic of a boiler unit's economy: the *efficiency* η_n . It is easy to see that if thermal losses are expressed as percentages, it is necessary to subtract these losses from 100 to obtain the value of boiler efficiency.

In generalized form the connection between the efficiency of a boiler operating with gaseous fuel (η_n) and its thermal losses is expressed by the formula

$$\eta_n = 100 - (q_1 + q_2 + q_3) [\%]. \quad (25)$$

Example 10. Find the efficiency of a boiler from the data in Examples 8 and 9. Take q_5 as equal to 1.5%.

In the preceding examples we found the values $q_2 = 9.6\%$ and $q_3 = 5.1\%$. According to formula (25) $\eta_H = 100 - (9.6 + 5.1 + 1.5) = 83.8\%$.

The value found for the efficiency shows that of all the available heat, 83.8% is consumed usefully — i.e., expended on the development of steam; the remaining 16.2% is not used, but goes to cover thermal losses of the boiler unit. A graph illustrating Example 10 (Fig. 16) gives a clear presentation of the thermal balance of a steam boiler.

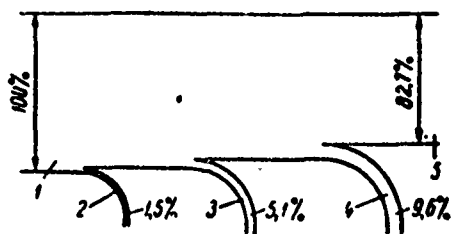


Fig. 16. Thermal balance of a boiler operating with gas fuel. 1 — chemically bound heat; 2 — losses to the environment; 3 — losses due to chemically incomplete burning; 4 — losses with stack gases; 5 — useful heat.

When a steam boiler operates on small loads the relative magnitude of losses to the environment will, as is known, be greater; with an increase in load this loss is reduced. From this we might draw the conclusion that it is necessary to attempt to organize the operation of a steam boiler in such a way that it will operate at the maximum possible load. However, such a conclusion is premature, since it is necessary also to clarify the way in which the other thermal losses of the boiler change with an increase in load.

The greater the load on the boiler the greater will be the quantity of gas burned in its furnace and, consequently, the more stack gases will be formed. Although the total quantity of heat

which is imparted by the gases to the heating surfaces will be increased, the increase will not be adequate. As a result the temperature of the stack gases grows with an increase in load. This gives an increase in losses with the stack gases which, in the end, invariably grows with an increase in load.

The conditions under which the gases mix with the air in the furnace become more complicated as the quantities of the two components are increased; this gives rise to the possibility of appearance of chemically incomplete burning. As a rule losses due to chemically incomplete burning are greater with large loads than with small ones.

As a result, changing the load on a steam boiler will influence the magnitude of its thermal losses and consequently will affect its efficiency in the manner shown on Fig. 17: at minimum boiler load (point a) the basic role is played by large losses of heat to the environment and the efficiency of the boiler is low. With an increase in load heat losses to the environment are immediately reduced, with this reduction being sharper than the increase in the remaining heat losses. Therefore the efficiency of the boiler grows and at a certain load (point b) reaches a maximum. With a further increase in load the heat losses with the stack gases and those due to chemically incomplete burning grow more sharply than heat losses to the environment are reduced and therefore boiler efficiency begins to drop from this point to achievement of the maximum possible load (point c).

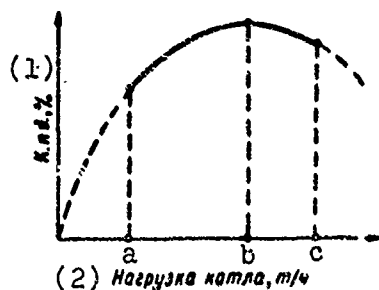


Fig. 17. Curve of steam boiler efficiency as a function of its load (with constant excess air factor α).

KEY: (1) efficiency, %; (2) boiler load, t/h.

Thus, every steam boiler has a certain load at which its efficiency reaches maximum value and which consequently is the most economical load. The operating conditions for a steam boiler should be organized in such a way that it operates at this most economical load for the greatest part of the time.

However, this rule does not exhaust the entire question of rational burning of gas in steam boilers. Correct organization of the air regime of furnace operation is extremely important. In the preceding section it was shown that the quantity of stack gases is increased with an increase in the excess air factor α ; consequently heat losses with the stack gases are also increased. However, an extreme reduction in α leads to the appearance of chemically incomplete burning, which causes heat losses which rise as the excess factor diminishes. To sum up, it seems that boiler efficiency has its maximum value at some certain value of α for every specific case (Fig. 18). With an increase in the excess air coefficient above this "optimum" value the losses with the stack gases grow more sharply than losses to incomplete burning are decreased; therefore the efficiency of the boiler unit is reduced. When the excess air factor is reduced from its optimum value the losses due to chemically incomplete burning grow more sharply than stack-gas losses are reduced, once again lowering the efficiency of the boiler.



Fig. 18. Graph of steam boiler efficiency as a function of the excess air factor α (at constant load).

KEY: (1) efficiency, %.

Methods of Analyzing Stack Gases During Complete and Incomplete Combustion

Each specific installation equipped with gas burners of a certain type has its own optimum value of the factor α — a value

which should be maintained during installation operation. But just how do we establish the factor α at which the furnace should operate, and how do we correct the air-supply conditions if this quantity deviates from its most economical value? In this connection an indispensable service is provided by *gas analyzers* - instruments used to carry out analysis of the dry portion of stack gases.

During combustion of any gas of constant composition the quantity of carbon dioxide in the combustion products will remain unchanged during a change in the excess air factor, while the quantity of other components of the dry portion of the combustion products will vary, reaching minimum values when the theoretically required quantity of air enters the furnace; in this case under conditions of complete combustion there will be no oxygen whatever in the combustion products, while nitrogen will be found only in an amount equal to 79% of the theoretically required quantity of air. With an increase in α all of the excess air enters into the combustion products and therefore the quantity of them is increased. Consequently, the percentage content of carbon dioxide in the combustion products has a maximum value during complete combustion of the gas with $\alpha = 1$ (i.e., with the theoretically required quantity of air), while it is reduced with an increase in α . In addition, the ratio of the percentage content of carbon dioxide in the dry portion of the combustion products to its maximum possible quantity is almost exactly equal to the excess air factor at which the combustion process is carried out.

We will clarify this extremely important position by means of a calculation for which the initial data will be those given in the example above. During the burning of 1 m^3 of gas of the composition which we selected above, 0.93 m^3 of carbon dioxide will be formed. If we assume that combustion proceeds with the theoretically required quantity of air (and is complete), the quantity of oxygen in the dry portion of the combustion products will equal

zero, while the quantity of nitrogen will comprise $0.79 \cdot 8.76 + 0.01 = 6.93 \text{ m}^3$ (see Example 7). Thus the total quantity of dry combustion products will be $V_{\text{cyx}} = 0.93 + 6.93 = 7.86 \text{ m}^3/\text{m}^3$, while the percentage content of carbon dioxide in it will equal

$\frac{0.93}{7.86} \cdot 100 = 11.9\%$. If we now assume that combustion proceeds with an excess air factor $\alpha = 1.2$, then, as was calculated above, the quantity of oxygen will comprise $0.37 \text{ m}^3/\text{m}^3$ and that of nitrogen will be $8.29 \text{ m}^3/\text{m}^3$. Then the total quantity of dry combustion products will be $V_{\text{cyx}} = 0.93 + 0.37 + 8.29 = 9.59 \text{ m}^3$, while the percentage content of carbon dioxide in them will comprise $\frac{0.93}{9.59} \cdot 100 = 9.7\%$.

Now by dividing the maximum possible content of carbon dioxide in the dry combustion products (11.9%) by 9.7%, we obtain the figure 1.23 — i.e., a quantity very close to the given excess air factor $\alpha = 1.2$.

For natural gases and other gases similar to them in composition the magnitude of the maximum possible content of carbon dioxide in dry combustion products can be taken as 12%. Then it is easy to establish just what the actual content of carbon dioxide should be in the combustion products when the furnace process is most economical. We will assume that with a given design of the gas burners the best results are obtained by burning gas with an excess air factor $\alpha = 1.2$. We will assume that with proper sealing of the boiler lining this quantity grows by 0.3 and consequently the optimum excess air factor in the stack gases $\alpha_{\text{yx}} = 1.5$. This means that the furnace air-supply conditions must be regulated in such a way that the actual content of carbon dioxide in the dry portion of the stack gases as indicated by the gas analyzer will comprise $12:1.5 = 8\%$. Deviation from this value to the lower side indicates a reduction in boiler efficiency due to increased heat losses with the stack gases, while deviation to the high side indicates a reduction in efficiency caused by an increase in heat losses due to chemically incomplete burning.

It should be borne in mind that the described method is approximate. More exact monitoring of the quality of combustion requires analysis of stack gases not only for carbon dioxide, but also for oxygen, carbon monoxide, hydrogen, and methane. If the contents of these components in the stack gases are known one can not only determine exactly the excess air factor, but also directly calculate heat losses due to chemically incomplete combustion.

The simplest and most convenient equipment for periodic monitoring of combustion are portable chemical gas analyzers of the GKhp-2 and GKhp-3 types (Orsat-Fisher) (Fig. 19). The first of three absorption vessels is filled with alkaline solution and serves for determination of carbon dioxide content in the dry combustion products; the second is filled with an alkaline solution of pyrogallol and is used to determine the oxygen content; finally, the third is intended for determination of the carbon monoxide which arises during incomplete combustion of the fuel. The third vessel is filled with an ammonium solution of copper monochloride. However, this solution is very unstable and therefore determination of carbon monoxide by the Orsat-Fisher instrument is unreliable. In practice the third vessel is most often either left empty and used as a backup or it is filled, like the second vessel, with a pyrogallol solution and is used for more complete absorption of oxygen.

The use of the Orsat-Fisher gas analyzer is suitable in those cases when combustion is virtually complete and the problem consists in determining the excess air factor so as to evaluate the correct setting of the furnace air conditions and the sealing of the gas ducts of the boiler or furnace. Stationary indicating and recording gas analyzers of various types are used for continuous monitoring of the composition of combustion products in such cases.

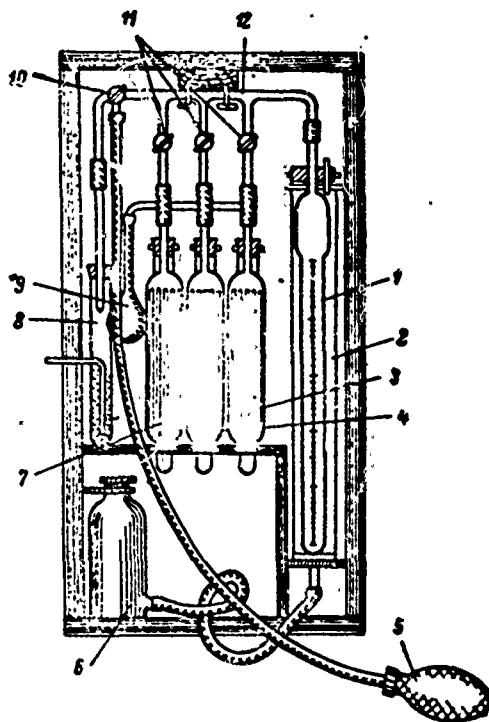


Fig. 19. The GKhp-3 gas analyzer (Orsat-Fisher). 1 - measuring burette; 2 - cylinder; 3 - absorption vessel with alkali; 4 - absorption with pyrogallol; 5 - bulb; 6 - pressure bottle; 7 - absorption vessel with ammonium solution of copper monochloride; 8 - filter; 9 - rubber bag; 10 - three-way valve; 11 - valve; 12 - manifold.

In those cases when fuel combustion is incomplete and the determination of losses due to chemically incomplete burning requires establishing the content of combustible components in the combustion products it is necessary to use other and more complex methods. Until approximately 1958 gas analyzers of the volumetric type were used almost exclusively for this purpose. The best known and most widely used is the VTI-2 gas analyzer. In this instrument (Fig. 20) the content of CO_2 and O_2 in a sample is determined by selective absorption of these components by liquid reagents, where the contents of CO , H_2 , and CH_4 are established by fractional burning of the remaining portion of the sample in a burning loop. In this case carbon monoxide and hydrogen burn at a loop temperature of 280°C , while methane burns at $850\text{--}900^\circ\text{C}$. The content of N_2 is determined by the difference method. This gas analyzer is sensitive to the temperature of the ambient air and therefore it must be installed in an area where there are no drafts and a constant temperature is maintained. The gas sample can be inserted in it with a pipette or with a Koro aspirator

[Translator's note. Exact spelling of "Koro" not found.].

However, accuracy of analysis on the VTI-2 is low. Even according to ГOST 6329-52 [ГОСТ = GOST = All-Union State Standard] a divergence of up to 0.2% between parallel results of gas analysis on this instrument is permitted during analysis by the absorption method (for CO_2 and O_2) and up to 0.3% during analysis by the burning method (for CO , H_2 , and CH_4). It has often been noted that the VTI-2 instrument often "detects" quantities of combustible components amounting to tenths of a percent in products of combustion which is known to be complete - i.e., where there are no such components at all. Along with this, an error of 0.3-0.35% in determining H_2 or CO or of 0.1% in determination of CH_4 will cause a deviation in the magnitude of losses due to chemically incomplete burning of approximately 1%. This means that the low accuracy of the VTI-2 leads to errors in determining these losses amounting to $\pm 1.5\%$ - i.e., any values obtained with it which are lower than 1.5% cannot be used, since they are below the level of instrument accuracy.

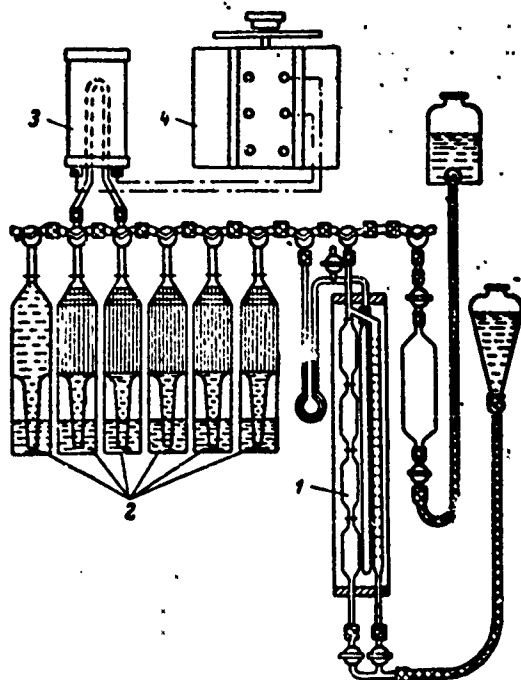


Fig. 20. Type VTI-2 portable gas analyzer for complete analysis. 1 - measuring burette; 2 - absorption vessels; 3 - burning loop; 4 - autotransformer.

At the present time furnace technology is extending itself on a broad front toward new and more exact methods of analyzing combustion products. One of these is the titrometric method, which provides incomparably high accuracy in determining the content of combustible components. In particular, this method is the basis for the design of the VTI-3 gas analyzer. The operating principle of this device consists in selective burning and accumulation of reaction products. A sample consisting of about 5 l of gas is first passed through filters which remove CO_2 , O_2 , and water vapor from it. The filtered gas is sent to a tube filled with iodic anhydride which is heated to $275\text{--}285^\circ\text{C}$. Selective burning of CO and H_2 occurs on the surface of this compound, after which the water vapor and carbon dioxide formed are successively absorbed by calcium chloride and barium hydroxide $\text{Ba}(\text{OH})_2$. Methane and other hydrocarbons are slow-burned in a tube connected below the first with cuprous oxide at a temperature of 850°C ; after this the CO_2 and H_2O formed are absorbed. The quantity of these reaction products is determined by titration with barium hydroxide and weighing of the tube with the CaCl_2 ; on the basis of the obtained results the quantity of H_2 , CO , and CH_4 burned is calculated. With qualified servicing by two laboratories the VTI-3 instrument gives an error of no more than 0.02% in a wide range of measured concentrations. However, due to the fact that the instrument is relatively cumbersome and because each analysis requires a considerable period of time (about 3 hours) it can hardly find use in the production of heat-engineering tests of boilers and is even less applicable in continuous monitoring of furnace operating conditions. Its application is recommended during measurements of large concentrations of combustible components (for example, during study of a burner), when high absolute accuracy is necessary for any reason.

A much more promising method is that of development chromatography, which is used at present by many scientific research

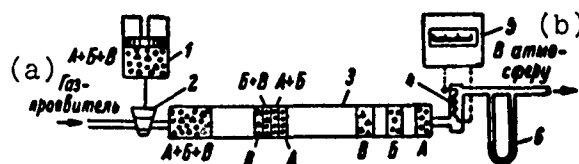


Fig. 21. Schematic diagram of the development method of chromatographic gas analysis. A, B, and B — components of the analyzed mixture to be determined. 1 — injector for sample introduction; 2 — device for introducing the sample; 3 — distributing column; 4 — detector; 5 — recording or indicating instruments; 6 — rheometer.

KEY: (a) Gas-developer; (b) To the atmosphere.

and troubleshooting organizations. Essentially this method consists in the physical separation of a gas mixture into individual components on the basis of differences in their physico-chemical properties. The device used for this purpose is called the chromatograph (Fig. 21). A flow of gas-developer is passed at constant velocity through distribution column 3, filled with granulated solid sorbent with a large reaction surface. The studied mixture containing components A, B, and B is introduced through doser 2 into the flow of developer by means of injector 1 and is filtered with it through the sorbent layer. As a result of the different rates of sorption and desorption of the mixture components differences arise in the rates at which they pass through the distributing column. At the beginning of the column the zones occupied by the components of the mixture coincide; then they begin to separate from one another, and at the end of the column they are completely separated. In this case different bands are spaced out along the column; these represent mixtures of each of the components with the gas-developer, while there is a flow of pure developer in the intervals between them. The component with the lowest sorption capability is the first to be

desorbed from the surface of the solid sorbent and therefore is the first to leave the distributing column. On the other hand, the component which is sorbed best of all on the surface of the sorbent is the last to leave the column. As the gas flow leaves the distributing column its thermal conductivity or heat of combustion is measured by means of a sensitive low-inertia attachment - detector 4. Platinum coils are used as the detector. Automatic recorder 5, connected to the detector, records the information concerning the composition of the moving gas flow and, consequently, the composition of the analyzed mixture; the information is expressed in the form of spikes on a base (null) line of the chromatogram, which is related to a flow of pure developer (Fig. 22). Measuring the height of the peaks (or their areas) permits determination of the volume content of individual components in the mixture. The component to which one or another peak belongs is established when the given component flows out of the column, since this time is a constant quantity for each gas.

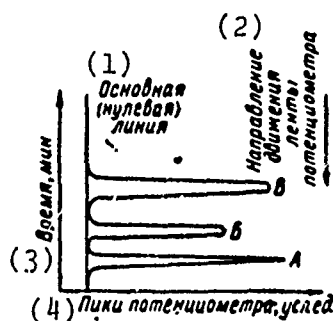


Fig. 22. Typical chromatogram of a mixture of components A, B, and C recorded on a potentiometer strip.

KEY: (1) Base (null) line; (2) Direction of potentiometer strip motion; (3) Time, min; (4) Potentiometer peaks, cond. units.

The time at which each component leaves the column and the dependence of the peak dimensions on the concentration of the appropriate component in the mix are established by preliminary calibration of the gas analyzer with the aid of the specially prepared control mixtures whose composition is known in advance. The calibration of the chromatograph consists in the construction for every component of a calibration curve, representing the dependence of the height of the peak on the concentration of the

appropriate component of the control mixture. As was established by A. A. Avdeyeva, the processing of chromatographs not by the heights of the peaks but by the areas included between the zero line and the corresponding peak is more complex and is connected with additional errors.

Today industry produces several designs of chromatographs, including some specially fitted for determination of the components of chemically incompletely burned H_2 , CO, and CH_4 in stack gases during the adjustment of combustion conditions. One such instrument, for example, is the KhGPM-2 gas analyzer, which has been developed and produced by the Ukrainian Institute for Planning of the Gas Industry. Unlike other designs, all elements of the KhGPM-2 (compressor, stabilized power-supply unit, adsorption column, detector, and rheometer) are arranged in a portable box, and the instrument can be carried by one man. Instrument sensitivity with a maximum dose of analyzed gas of 10 ml composed of all combustible components is 0.005%; the analysis time is about 4 min.

CHAPTER IV

FLAME PROPAGATION IN STATIONARY GAS-AIR MIXTURES

Chain Reactions in a Gas-Air Mixture

Very frequently the physical senses are inadequate for correct analysis of the essence of some natural phenomenon, even one which seems simple at first glance. A very ordinary and common phenomenon which is nonetheless very complex is the combustion process. Fire has always played a huge role in human life. The ability to confine the fiery element and subordinate it to his service helped Man to emerge victorious in the battle with a powerful and hostile natural world and to create contemporary society, with its rich and varied culture. Even without a correct understanding of the nature of fire both ancient peoples and many populations who had already taken long strides down the road to cultural development frequently idolized it, worshiped it, and tried to propitiate it with sacrifices. In the Middle Ages science regarded the combustion process as the liberation from the burning body of the so-called phlogiston - some sort of fantastic substance possessing "negative" weight. This idea was supported for a very long time, right up to the end of the Eighteenth Century. Then scientists realized that combustion is the process of the combination of a combustible material with oxygen; but all the same, fire remained a mystery. Only contemporary science, equipped with the most modern instruments for research, is able to

penetrate this riddle and correctly describe the essence of the combustion process. The theory of chain reactions, which constitute the basis for the entire combustion process, was developed only a few decades ago, mainly thanks to the work of Soviet scientists (Academician Semenov and his students).

The essence of the combustion processes is very complex. We will limit ourselves at first to consideration of the basic phase of the combustion process - the properly chemical reaction between any combustible gas and atmospheric oxygen. For simplicity we will use hydrogen, whose molecule has the simplest structure and for which therefore the process of chemical reaction is least complex.

Not even the most powerful microscope can allow us to see the molecules of which the gas consists, to observe their behavior and thus to observe the events which may (and actually do) occur in the space occupied by molecules of hydrogen when even a single molecule of oxygen appears in it. Therefore we will consider common sense and imagination to be the basic tools for our investigation.

We will prepare a mixture of hydrogen with that quantity of air which is theoretically necessary for its complete combustion. Such a mixture is called *stoichiometric*. In order for a mixture of hydrogen with air to be stoichiometric it is necessary that the volume quantity of oxygen in the air used be two times less than the volume quantity of hydrogen.

A simplified concept of gas molecules as being small elastic balls which move at random at great velocity throughout the entire space available to them and which fly off in different directions after collisions until collisions occur with others of the same types of balls enables us to explain and clarify the basic physical properties of gases. We can state that the obtained mixture

will be uniform, since each of the component gases in it (hydrogen, oxygen, and nitrogen) will be distributed uniformly throughout the entire volume of the vessel. However, for deeper analysis of processes in a gas-air mixture, examining not only the physical but also the chemical phenomena, such a simplified presentation is inadequate. Now we must remember that the molecules of gases are not actually spheres. They are actually complex formations consisting of individual atoms. In our case each molecule (hydrogen, oxygen, and nitrogen) consists of two atoms more or less strongly connected to one another by the forces of mutual attraction.

We will consider that the mixture is at ordinary or room temperature. This means that the average velocity of the molecules of all gases in the mixture is small. However, it does not mean that there are no molecules in the mixture with high velocity and consequently, a high reserve of kinetic energy. Actually any vessel, however small, contains many billions of molecules; among them there will always be found some whose speed of motion is very small as compared with other molecules, and also others with relatively very high velocities.

If molecules with low velocities collide with one another no substantial consequences ensue: they simply bounce away from one another. The situation is different with that comparatively small number of molecules whose velocity is relatively very great. For them a collision can be fatal. The force of the impact of such a molecule on another one is so great that the bonds between its atoms cannot maintain themselves and the molecule breaks down into individual atoms. Besides this, the energy which was expended on joining the atoms into the molecule is liberated during this breakdown and is added to the kinetic energy possessed by the molecule prior to collision. The fragments of the decomposed molecule become "active." Their energy is so substantial that when they collide with whole molecules they break them apart;

in its turn, this leads to the creation of new "active centers," as such molecular fragments are called, possessing a great reserve of energy. Along with this, when active centers collide with one another they may cease their individual existence, uniting into new whole molecules, since they possess an adequate energy reserve to accomplish this.

Nitrogen takes only a passive part in all of the molecular transformations described above. Colliding with the nitrogen molecule, a molecule of hydrogen or oxygen may be destroyed, but the nitrogen molecule remains undamaged. Therefore nitrogen is called an inert gas, since the bond between its atoms in its molecules is extremely strong and the latter are very stable.

It is true that at high temperatures in a flame nitrogen oxides are always formed (NO , N_2O_3 and NO_2), but the quantity is so small that they can be ignored altogether. Thus, during consideration of a stoichiometric mixture of hydrogen with oxygen the nitrogen contained in it can be simply dropped out of the calculation.

As regards to molecules and atoms of hydrogen and oxygen, collisions between them lead to very different results. For example, an active atom of hydrogen which collides with the molecule of oxygen may split off one atom from it and form an unstable compound - the hydroxyl group OH - with the remaining one; in exactly the same way an active atom of oxygen upon collision of the molecule of hydrogen may split off one atom from it and form a hydroxyl group with the other.

Among all such collisions special attention should be paid to those which result in the formation of a molecule of water vapor (for example, if a hydroxyl group encounters a molecule of hydrogen it may split off one hydrogen atom from it and may form a stable molecule of water vapor with the other one). This

leads to a gradual change in the composition of the mixture; the water-vapor content grows gradually at the expense of a reduction in the hydrogen and oxygen contents.

At first glance the totality of all possible transformations with molecules and their fragments should be completely random. However, in actuality one of them is the most probable and the others are less probable, and since a great number of such transformations occur in a mixture the actual ratio between their quantities is found to be a determined one. Actually, when we are dealing with a very great number of events those ratios between them which are most probable become completely reliable. The ratio between the probabilities of individual chemical transformations in a mixture of hydrogen with air is such that the most probable (and therefore most frequent in reality) event is the series of transformations depicted schematically on Figure 23. Free hydrogen atom 1, colliding with oxygen molecule 4, breaks off one atom 2 from it and occupies its place, forming hydroxyl particle 5 with the remaining oxygen atom. Colliding with hydrogen molecule 3, the hydroxyl particle breaks off one hydrogen atom from it, transforming it into a new active center, and forms a stable compound with a remaining atom - a molecule of water vapor 6 which in the majority of cases will drop out, as it were, from the game (since its destruction requires a very great deal of energy - more, as a rule, than the particles located in the mixture possess). Now we will trace the fate of oxygen atom 2, which appeared as the result of the first collision. Colliding with yet another molecule of hydrogen, it splits off one atom from it - this becomes a second active center - and forms a hydroxyl particle with the other; in its turn this hydroxyl group collides with a molecule of hydrogen and, splitting off one atom from it and creating a third active center, it forms one molecule of water vapor with the remaining atom.

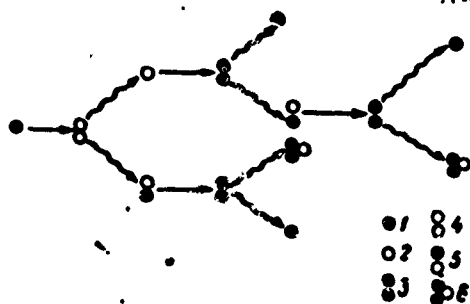


Fig. 23. Diagram of a series of transformations excited by an active center in a hydrogen-air mixture.

Thus the series of transformations caused by the hydrogen atom formed as a result of thermal motion of molecules and existing as an active center terminates in the formation of two molecules of water vapor and three new active centers (free hydrogen atoms). Such a series of transformations can be depicted in simplified form by the diagram shown on Fig. 24.



Fig. 24. Simplified diagram of the series of transformations excited by an active center in a hydrogen-air mixture (for designations see Fig. 23).

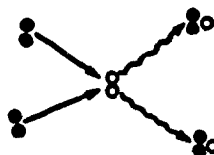


Fig. 25. Diagram of a triple collision (for designations see Fig. 23).

Of course, we should not think that no other sequence of particle interaction can exist in a mixture. For example, the case when two molecules of hydrogen collide simultaneously with one molecule of oxygen is not excluded. If the total energy of all three of these molecules is sufficiently great the collision terminates in the formation of two molecules of water vapor (Fig. 25). However, no calculations are necessary for us to realize how low the probability of such a variant is compared with the sequence of simple collisions just described. Thus,

the probability of the latter is so much greater than any other possible scheme of transformation that all remaining variants can simply be ignored in the calculations as being uncharacteristic for the considered gas-air mixture.

The fate of the three new active centers may be different. Each of them may either cease to exist as a result of combination with another similar active center into a stable hydrogen molecule, or it may stimulate the beginning of a similar series of transformations. The question of the conditions under which the first outcome is more probable and those under which the second is more likely to occur will be considered below. Now it is important to establish that if each of the active centers after the first series of transformations gives rise to a similar following series, a whole chain of transformations is formed with multiplication of active centers occurring in each link along with the formation of stable molecules of the final reaction product (two molecules of water vapor). As a result a new substance is accumulated in the mixture and the content of the initial gases is correspondingly reduced.

Chemical transformations of the described nature are called *chain reactions*. The leading role of active centers, multiplying in each link of the transformation, is a characteristic feature. Reactions of combining of oxygen and with other combustibles - carbon monoxide, methane, and heavy hydrocarbons - are a similar type. It is true that these reactions are more complex than those in the case analyzed above. The more complex the molecule of combustible gas the more different intermediate substances may appear and disappear in each link of the chain reaction and the more complex will be the sequence of individual transformations within this link. However, the basic regularities of the process described above will remain the same.

Ignition Temperature and Thermal Explosion of a Gas-Air Mixture

If it were possible to calculate the number of active centers existing at any given moment in a gas-air mixture, we would find that at relatively low temperatures (for example, at room temperature) their number will, generally speaking, be negligible as compared with the quantity of other particles - mainly stable molecules. A second and no less important conclusion would be the fact that at different moments of time their number remains approximately constant. A part of the active centers will be formed due to the thermal motion of molecules. Another part is generated by the chain reaction, since in each link of this reaction several new active centers will be formed. However, along with this there is a continuous process of destruction of active centers; some of them cease to exist after giving rise to the beginning of a new chain reaction, while others simply combine back into molecules of the initial gas. In other words, *at low temperatures a certain equilibrium exists in a mixture between processes of generation and destruction of active centers; as a result their concentration in the mixture remains approximately constant.* Under low-temperature conditions only a few of the active centers give rise to chains, and those chains which are formed are quickly broken due to the "death" of all of the active centers generated in them.

An idea of the course of a chain reaction in a hydrogen-air mixture at low temperatures is presented by the diagram shown in Fig. 26. Active center 1 excites a typical sequence of transformations, forming the first link of the considered chain. Of the three active centers formed in this link one perishes, while the remaining active centers excite similar sequences of transformations. Thus another two links of our chain are formed - i.e., the chain branches. In its turn the new active center

of the left branch gives rise to the following chain, while the remaining two active centers perish. On this link the left branch of the chain is broken, since all of the active centers generated in it die off.

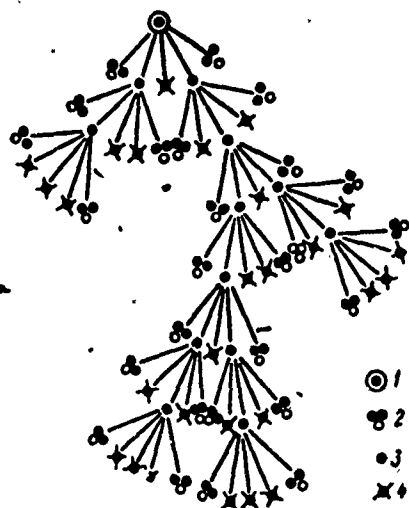


Fig. 26. Chain reaction in a hydrogen air mixture at low temperature. 1 - active center (hydrogen atom) generating a chain reaction; 2 - stable molecule of the final reaction product (water vapor); 3 - active centers (hydrogen atoms) continuing the chain reaction; 4 - active centers (hydrogen atoms) at which the chain is broken.

In the same way, the right branch of the chain is continued by one active center, and then branches at two active centers. The active center to the right gives rise to still another link, on which the branch of the chain is broken, while the middle branch of the chain is continued and then in turn is split by two active centers. After two transformations the reaction is finally broken. It goes without saying that the described scheme is only an illustration showing how breaking, continuation, branching of a chain occurs in the course of a chain reaction. The entire sequence of links given in it is completely random.

Thus, at low temperatures the majority of active centers arising during the thermal motion of molecules perish without giving rise to a chain reaction. The chains which do arise are frequently very short-lived (see Fig. 26). Therefore the formation of molecules of the final reaction product is so sluggish that the composition of the gas-air mixture is virtually unchanged for practical purposes. For example, no matter how many observations

we make of a cold hydrogen-air mixture, we will not notice traces of water vapor in it if there was none present during the formation of the mixture. The accumulation of water vapor in a quantity large enough to be detected requires a tremendous period of time, indicated by calculations to be several million years.

The situation is different with regard to development of the interaction process between a combustible gas and oxygen in a gas-air mixture at high temperature, when the rate of formation of active centers begins to exceed the rate of their disappearance: the majority of the newly formed active centers cause a series of transformations in which one or several molecules of inert final product appear (water vapor or carbon dioxide), along with several new active centers. Each of the latter in turn gives rise to molecules of final product and new active centers, and so on.

We must not forget that during the transformation of a combustible gas and oxygen into final products a large amount of energy is liberated; this energy is picked up by molecules of the reacting gases. Their velocity is increased, which causes an additional increase in the rate of formation of active centers. The reaction becomes self-accelerating and as a result of the interaction between the combustible gas and oxygen it is developed at a high rate and instantaneously, within thousandths of a second, it covers the entire volume of the gas-air mixture.

Thus, there are two conditions of the reaction between a combustible gas and oxygen in a gas-air mixture: the low-temperature regime, with which the reaction, although it does occur, is so sluggish that for practical purposes it cannot be detected; and the high-temperature regime, during which it proceeds so vigorously that it is completed almost instantaneously. During the low-temperature reaction, called *oxidation*, heat is liberated in a negligible amount and, since it is gradually dissipated into the ambient medium, the temperature of the mixture is not changed.

During the high-temperature reaction, called *burning*, heat is liberated vigorously and in large quantities; since it cannot dissipate into the environment because of the extremely short reaction time and is expended mainly on heating the final products, burning is accompanied by a sharp elevation in temperature.

It is obvious that some intermediate transition regime must exist between these two conditions; in this transition regime the process of branching of the chains of the chain reaction (i.e., generation of several new centers by one active center) is immediately compensated by the process of chain breaking (i.e., the death of all new active centers except one, which continues the chain). This transition regime is called the *ignition of a gas-air mixture*, and the transition temperature corresponding to it is called the *ignition temperature of the mixture*.

Thus, when a cold gas-air mixture is heated no noticeable changes occur in it at first; then, when the ignition temperature is reached, there is a virtually instantaneous combustion reaction accompanied by the liberation of a large quantity of heat. The existence of an ignition temperature and of two regimes which differ from one another in principle (low-temperature oxidation and high-temperature burning) is the distinguishing feature of reactions of combustible gases with oxygen in gas-air mixtures.

We will assume that the walls of a vessel containing a gas-air mixture are completely impervious to heat. Then no matter how small the quantity of heat liberated in the mixture, it will gradually be accumulated inside the vessel and the temperature in the mixture will be raised. The reaction becomes ever more and more intense, and in the end the process is terminated by ignition or burning of the entire mixture. Under real conditions it is impossible to achieve such complete thermal insulation

of a vessel, and therefore the process of accumulation of heat in it is always accompanied by the process of loss of heat to the environment. In this case the magnitude of the heat losses can be considered approximately proportional to the difference between the temperatures of the mixture and of the vessel walls. It is easy to see that under these conditions there is established, as it were, a thermal equilibrium in the vessel; here the quantity of heat liberated during the reaction is equal to the heat loss through the walls and, consequently, after reaching a certain level the temperature of the gas-air mixture is stabilized. This reasoning can be clearly confirmed by means of the graph presented on Fig. 27.

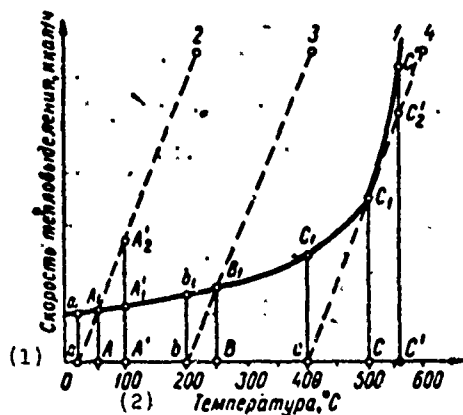


Fig. 27. Graph of the thermal equilibrium of a gas-air mixture. KEY: (1) Rate of heat liberation, Cal/h; (2) Temperature, °C.

We know that at low temperatures the rate of oxidation of a combustible gas in a mixture is negligible, but with an increase in temperature it nonetheless increases. The rate of heat liberation - i.e., the number of kilocalories of heat liberated by the mixture per unit time (hour) - changes accordingly. This relationship is depicted on the graph by the initial segment of curve 1, which passes close to the horizontal axis and is deflected upward very weakly as the temperature is increased. When the mixture is heated to the ignition temperature the reaction rate rises smoothly but very quickly, so that curve 1 representing heat liberation turns sharply and rises upward.

Here it is important to take note of the following circumstance. The reader already knows that after ignition the combustion reaction is completed almost instantaneously; therefore he might expect that curve 1 would have a break at the point corresponding to the ignition temperature and then would rise almost vertically. This would be so if time were plotted along the horizontal axis. The dependence of the reaction rate, and, consequently, the rate of heat liberation on temperature has a different character and is expressed as a smoothly rising curve.

We will now assume that the mixture is placed in a vessel whose walls have a temperature corresponding to point a (according to the scale on the axis it equals 20°C). At this moment the rate of heat liberation in the mixture will correspond in magnitude to vertical segment $a - a_1$, as follows from the meaning of the temperature liberation curve 1. At this moment the heat transfer to the walls of the vessel will be zero, since the temperatures of the mixture and the walls are identical. But nonetheless a reaction is occurring in the mixture and consequently heat is liberated in it. Therefore the mixture begins to be gradually heated. As soon as a temperature difference arises between the mixture and the walls heat exchange from the mixture to the walls begins. The rate of heat exchange is proportional to this difference in temperature; consequently the quantity of heat lost by the mixture is depicted as a function of its temperature by line 2, which rises upward with a certain constant slope. The constant slope of line 2 - i.e., its straightness - shows the degree to which the temperature differences increase and by how many times the quantity of heat loss by the mixture is increased. The temperature of the mixture will rise until thermal equilibrium is established - i.e., until the quantity of heat lost by the mixture becomes equal to the quantity of heat liberated by the mixture. It is obvious that this will occur at the moment corresponding to point A_1 , where lines 1 and 2 intersect. The

temperature established in the vessel will be higher than the wall temperatures. On the chart it corresponds to point A (about 50°C on the scale). The thermal equilibrium will be stable. Actually, we will assume that by using external heat we heat the mixture to a temperature corresponding to point A'. But then the quantity of heat lost by the mixture will be depicted by segment A' - A'₂, while the quantity of heat liberated by the mixture is represented by segment A' - A'₁. It is clear that the mixture will lose more heat than it obtains and therefore it is cooled to the previous stable temperature, corresponding to point A.

We will now assume that the walls of the vessel are heated to a temperature corresponding to point b (200°C on the graph). Naturally in this case the mixture will be heated to the same temperature. The rate of heat liberation grows to a quantity corresponding to segment b - b₁. In the first moment no heat exchange occurs from the mixture to the walls, since their temperatures are identical. Therefore self-heating of the mixture begins and its temperature begins to rise. Simultaneously an increase in heat exchange to the walls begins; here the appropriate relationship between the rate of heat exchange and mixture temperature is depicted by straight line 3, parallel to line 2 but beginning from point b. It is not difficult to see that the state of stable equilibrium in this case will be achieved at a temperature corresponding to point B (260°C on the graph). As is clear from this, an increase in the temperature of the vessel walls increases the temperature of stable thermal equilibrium of the mixture.

We will now heat the vessel walls in such a way that the line of heat transfer will become tangent to the line of heat liberation 1. On our graph this corresponds to heating of the walls up to a temperature corresponding to point C (about 400°C on the scale). In this case heat-transfer line 4 touches the heat liberation line 1 at point C₁. Reasoning along the same lines

as in the preceeding cases, we can establish that the mixture is heated due to heat liberation up to a temperature corresponding to point C (500°C on the scale). At this temperature the state of thermal equilibrium will be established in the mixture, since the rate of heat liberation will become equal to the rate of heat transfer. But will such thermal equilibrium be stable? In order to answer that we heat the mixture to a somewhat higher temperature - for example, to a temperature corresponding to point C' (560°C on the scale). Then the rate of heat transfer becomes equal to the segment $C' - C'_2$, while the rate of heat liberation will equal segment $C' - C'_1$, which is greater in value. This means that after such a thermal "jump" the mixture does not return to the initial temperature corresponding to point C', but it begins to accumulate heat and is heated until it ignites and burns.

Thus, in order for the mixture in a vessel to remain unignited the temperature of the vessel wall should be lower or, in the extreme case, equal to a temperature corresponding to point C. With the slightest excess of this temperature self-heating of the mixture sets in, followed by ignition.

It is self-evident that the greater the thermal conductivity of the vessel walls and the better they are cooled by ambient air, the steeper will be the lines of heat transfer and, consequently, the higher will be the temperature of the wall at which self-ignition of the mixture will occur. This consideration is a good explanation of the fact that with different experimental conditions the ignition temperature of the mixture is found to be different, while the specialized literature contains completely contradictory data on ignition temperatures of different combustible gases in mixtures with air.

Uniform Propagation of a Flame in a Cold Gas-Air Mixture

In the preceding section it was shown that combustion of a fuel gas mixed with air in stoichiometric ratio requires that such a mixture be heated up to the ignition temperature. If the quantity of the mixture is substantial this requires a large expenditure of heat, since the ignition temperature always amounts to several hundred degrees. However, it is possible to organize the situation in such a way that the mixture will heat itself and there is no need for expenditure of heat for this purpose from some outside source. For this it is sufficient merely to ignite the mixture by introducing a burning match, incandescent metal, etc. Despite the fact that the quantity of heat liberated in this case is negligible and in itself incapable of providing any substantial rise in the temperature of the entire mixture, in the end the entire mixture is completely burnt. This occurs because a gas-air mixture (like any other physical body) possesses a definite and also limited heat conductivity.

The essence of this property is most easily explained by using the example of a solid body - for example, a metallic rod. If such a rod is heated from one end we can see that a process of propagation of heat occurs in it; this is accompanied by a gradual rise in temperature over the entire length of the rod. Finally not only the heated end of the rod is warmed up, but also the opposite end. This is explained by the fact that the molecules of the heated end of the rod, like those of any other solid body, are in continuous oscillatory motion. When energy is obtained from a source of heat the intensity of their oscillations is increased; as is already known, this leads to an increase in temperature on the heated end. Colliding with molecules in the neighboring segment, they impart to them a portion of acquired energy and this leads to an increase in temperature of the neighboring section of the rod. In their turn the molecules of

this segment collide with molecules of the following segments, impart to them a portion of the obtained energy, and so on. Heat transfer occurs, as it were, by a relay race - the molecules do not change their average position, but they transmit thermal energy to one another from the heated end of the rod to the cool end.

In gases molecules do not retain their average position, but are in continuous chaotic motion, continuously colliding with one another and flying off in various directions. Therefore the thermal conductivity of gases is conditioned not only by transfer of energy from one molecule to another, neighboring one, but also by direct transportation of energy by molecules of the heated layer of gases which penetrate into the neighboring, unheated layer. Although the speed of molecules in a gas is very great (several kilometers per second), the continuous collisions constantly alter the direction of their motion. Therefore the rate of penetration of molecules from one layer into another is generally not great and the thermoconductivity of gases is low as compared with that of solid bodies, in which the average distances between molecules are substantially less. For example, the thermal conductivity of hydrogen (which possesses the greatest thermal conductivity among gases) is several hundred times lower than that of copper. The above is completely applicable to the thermal conductivity of mixtures consisting of a combustible gas and air. It is easy to understand that it is precisely the well-known difficulty in propagation of heat in the volume of the gas-air mixture which ensures the possibility that it will burn even if its temperature is not particularly great. Actually, let us imagine that the heat from the ignition source is propagated instantaneously over the entire volume of the mixture and uniformly distributed in it. Then the insignificant quantity of heat liberated by the ignition source would not be

adequate to heat the entire mixture by even a few degrees. Naturally there would be no ignition and the mix would not burn.

The process which actually occurs is entirely different. If an incandescent body is introduced into a gas-air mixture and if its temperature is higher than the ignition temperature of the mixture, the extremely thin layer of mixture directly adjacent to its surface is swiftly heated to the ignition temperature and it will burn even though the subsequent layers have only begun to be heated because of the limited thermal conductivity of the mixture. In this case the molecules of combustible gas and atmospheric oxygen in this layer disappear and are replaced by "hot" (i.e., high-speed and consequently high-energy) molecules of gaseous combustion products. The quantity of heat which is liberated is sufficient to heat the combustion products formed up to a temperature on the order of 2000°C and consequently it is sufficient to heat the next layer to the ignition temperature. Penetrating into the next layer and imparting a portion of their energy to it, the combustion products heat it up to the ignition and burning temperature. In this sequence the process expands from layer to layer, encompassing an ever greater volume of the gas-air mixture until the entire mixture burns.

Thus, the factor which causes the propagation of the burning process in a cold gas-air mixture is the thermal conductivity of this mixture - i.e., its ability to transfer heat from layer to layer. Along with this we should emphasize that it is precisely because this thermal conductivity is not very great that conditions arise which guarantee the possibility of the actual appearance of the combustion process.

The process of combustion of a cold gas-air mixture is most easily observed in the instrument depicted on Fig. 28. It consists of glass tube 4, one end of which is sealed, and which together with valve 2 is connected to buffer bottle 1. Electric igniter 3

is installed in the tube in direct proximity to the valve. The tube is filled with a mixture of combustible gas and air and the buffer bottle is filled with simple air or with some inert gas - e.g., carbon dioxide or nitrogen. The buffer bottle has a volume which is 80-100 times greater than the volume of the tube itself and it serves to ensure constant pressure in the instrument. When the mixture is triggered by the igniter, a thin layer of hot gas is formed next to it; this is called the flame front. It travels gradually along the tube in the direction of its sealed end. Since the combustion products formed behind the flame front have a high temperature, when the valve is closed the pressure in the tube will be increased as more products are formed. In order to prevent this the valve is opened and the excess combustion products pass through it into the buffer bottle.



Fig. 28. Instrument for observation of the process of flame propagation.

The flame front has an almost flat shape, but close to the walls (through which heat transfer into the environment occurs) a convex meniscus is formed. The speed at which it travels along the tube remains constant, in any case so long as the buffer bottle maintains a constant pressure in the tube. Naturally, the magnitude of the flame-front speed will differ for different gas-air mixtures. If the mixture possesses high thermal conductivity the transfer of heat from layer to layer will occur more rapidly and the flame front will be displaced at a higher speed. One can consider that the thermal conductivity of the mixture is the basic factor governing the rate of travel of the flame front or, which is the same thing, the rate of flame propagation.

However, when the diameter of the tube is changed the propagation rate of a flame in gas-air mixtures of identical composition will also be changed: it is increased with an increase in tube diameter and reduced with a reduction in this

diameter. The reason for this is as follows. The heat which is liberated in the layer of reacting mixture is not entirely directed toward heating the next layer. Part of it is lost to the environment through the walls; here the fraction of lost heat is the greater, the smaller the diameter of the tube. By reducing the tube diameter we introduce a continuously increasing difficulty for the process of heat transfer from one layer of mixture to another and thus increase the fraction of heat which is transmitted out through the wall. In connection with this the flame propagation rate is also reduced. With a further reduction in tube diameter a position inevitably arises in which the thermal losses through the walls become so great that the heat remaining is insufficient to heat the layers, one after another, up to the ignition temperature and the flame will not propagate in the tube at all.

For every combustible mixture there is a "critical" diameter at which propagation of a flame in the tube becomes impossible due to the extreme cooling of the mixture by the walls. Thus the critical tube diameter is about 0.9 mm for a stoichiometric mixture of hydrogen and air and about 3.5 mm for a stoichiometric mixture of methane with a layer.

Just how should the propagation rate of a flame change in a tube if the diameter is increased? We will first consider the conclusions which we reach by simple logical reasoning and then we will turn to data obtained from experiments. The fraction of heat which is lost through the walls is reduced with an increase in diameter and in the end becomes negligibly small. This, however, does not mean that the flame propagation rate will increase infinitely. It should grow, but it will grow ever slower and slower, since in complete absence of cooling by the walls the propagating flame is retarded by the limited thermal conductivity of the mixture. We will construct the graph of flame propagation rate in a tube as a function of tube diameter,

plotting the tube diameter along the horizontal axis and the corresponding flame propagation rates along the vertical (Fig. 29). This relationship is depicted by curve 1, which originates from the horizontal axis at a point corresponding to the critical diameter (at the critical diameter the flame propagation rate equals zero and therefore the initial point lies on the horizontal axis). The curve rises upward first steeply and then more smoothly, gradually approaching horizontal line 2, which corresponds to the maximum rate of flame propagation without limitation by the cooling influence of the tube walls and determined only by the thermal conductivity of the mixture and other factors inherent to the mixture itself - e.g., the heat of combustion of the gas and its composition.

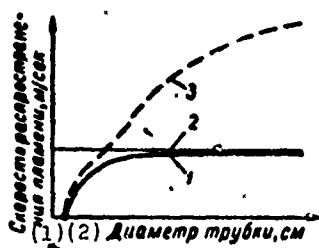


Fig. 29. Curve of flame propagation rate as a function of tube diameter.

KEY: (1) Flame propagation rate, m/s; (2) Tube diameter, cm.

Since losses of heat through the walls are reduced with an increase in diameter only with respect to the quantity of heat liberated in the flame front, and in fact may even grow in absolute value, curve 1 only approaches horizontal line 2, and does not reach it even at very large diameters. We must not forget however, that the obtained curve is the result of logical reasoning. In reality, as experiments show, the growth in the flame propagation rate with an increase in tube diameter has a different character. As indicated on Fig. 29 by broken line 3, the flame propagation rate grows substantially more rapidly than we would assume and quickly exceeds the maximum value corresponding to horizontal line 2. This occurs because during displacement of the flame front in a hot mixture the latter does not remain immobile: vortex flows arise in it, forcing stretching and bending of the

flame front. As a result the surface of the flame front is increased and can become much greater than the cross-section area of the tube. For example, in a tube 5 cm in diameter (whose cross-section area is about 20 cm^2) during combustion of a mixture of methane with air the surface of the flame front can vary within the limits 60 to 117 cm^2 - i.e., it can amount to 3-6 times the area of the tube cross-section. It is easy to see that if the thickness of the combustion zone is identical both with a flat and a stretched and distorted flame front, the rate of combustion of the mixture will change in the same proportion. But even if the mixture in the tube actually burns, let us say, 5 times more quickly than we assumed, this means that the actual propagation rate of the flame will be 5 times greater than the assumed rate.

Thus, the formation of vortices in an immobile combustible mixture, becoming ever more intense with an increase in tube diameter, causes a substantial increase in the flame propagation rate as compared with those values which would be observed in the absence of vortices and with a flat combustion front.

The instrument described above is used during experimental determination of flame propagation rates by the so-called static method. Essentially this method consists of the following: the position of the flame front traveling along a tube is fixed after a certain time interval by means of cinematography. Then the distance between two neighboring positions of the flame front is divided by the corresponding time interval, which gives the value of the flame propagation velocity.

As was shown, the results of determining the flame propagation rate by the static method depends strongly on the diameter of the tube and, consequently, cannot objectively characterize the properties of the combustible mixture itself. Nonetheless, data obtained in this way are frequently used in engineering calculations; in order to match results from different studies, the

accepted practice is to carry out studies in tubes 1 inch in diameter (or 25.4 mm).

The idealized process of flame front displacement in a combustible mixture, caused only by thermal conductivity of the mixture and not distorted by either heat losses through the walls or eddying of the mixture, is called *normal propagation of a flame*, while the speed of this displacement, depending only on thermal conductivity and other physicochemical properties of the mixture itself (in contrast to the rate of uniform flame propagation, which depends on external factors - losses through the walls and due to eddying), is called *normal rate of flame propagation*. It is obvious that on Fig. 29 the distance from the horizontal axis to horizontal line 2 actually gives the magnitude of this normal rate of flame propagation.

The concept of the normal flame propagation rate can be approached by another method. Leaving the diameter of the tube unchanged, we will vary the heat transfer through its walls by reducing their thermal conductivity. The smaller the fraction of heat liberated in the flame front which is passed out through the walls to the environment, the greater will be the rate of uniform propagation of the flame. At the limit at which the thermal conductivity of the walls becomes equal to zero and, consequently, all of the liberated heat will be consumed in heating the mixture ahead of the flame front, the propagation rate of the flame front will reach its maximum value - equal, obviously, to the normal rate of flame propagation.

Thus, the normal rate of flame propagation can be defined as *that rate at which a flame is propagated in a combustible mixture which is immobile and which is not perturbed by eddies, under the condition of total thermal insulation of this mixture and is with strictly constant process pressure.*

Explosive Limits of Gas-Air Mixtures

When the flame front is displaced along a tube filled with a gas-air mixture a space filled with products of completed combustion is left behind it. The temperature of these products is very great and therefore the heat liberated in the combustion zone cannot propagate in a direction opposite to the flame-front motion, since heat is able to transfer only from more heated bodies to less heated bodies.

On the other hand, the layer of gaseous mixture reacting in a combustion zone has already been heated by the preceding layer to the ignition temperature and then during ignition to a still higher temperature. Therefore only a small fraction of the heat which is formed is required to heat the products formed in the combustion zone up to their final temperature. Naturally, all of the remaining heat strives to move ahead to the layer of mixture immediately adjacent to the flame front. The flow of heat forming the leading edge of the flame-front motion will be more intensive and, consequently, the rate of flame propagation will be the greater the higher the temperature of the flame front; it depends on the quantity of heat liberated during combustion of the mixture. Therefore the rate of flame propagation depends essentially on the proportions in which the combustible gas is mixed with air.

We will clarify this by comparing three different gas-air mixtures in which a combustible gas with a heat of combustion of 8000 Cal/m^3 is mixed with air in different proportions. We will assume that the total combustion of 1 m^3 of this gas theoretically requires 9 m^3 of air and that the mixtures have the following ratios. mixture 1, 1:9 (gas-air), mixture two 0.5:9.5, and mixture three 5.5:4.5 (figures in m^3). In other words, in the first mixture the content of combustible gas comprises 10 vol. %;

in the second mixture it is 5 vol. % and in the third, 55 vol. %. It is easy to see that during complete combustion of 10 m^3 of the first mixture, 8000 Cal will be liberated; complete combustion of the same quantity of the second mixture will release only 4000 Cal (since there is only half the gas in it as in the first) and, finally, complete combustion of the same quantity of the third mixture will also liberate only 4000 Cal (although there is plenty of gas in it, there is only sufficient air to burn 0.5 m^3 of the gas). From this we can conclude that the rate of flame propagation in such mixtures will also be different. It will be greater in the first mixture (stoichiometric) and less in the second and third mixtures.

In general, the obtained conclusion is confirmed by experiment. The highest flame propagation rate occurs in mixtures whose composition is close to stoichiometric, while enriched mixtures (i.e., an increase in the combustible gas as compared with the stoichiometric ratio) give reduced flame propagation rates. The same is true in lean mixtures (i.e., with a reduction in the content of combustible gas as compared with the stoichiometric): in these mixtures the flame propagation rate is reduced.

The only nonconformity between reality and our reasoning is found in the fact that the highest rate of flame propagation is observed at a mixture composition which is not strictly stoichiometric, but which contains a certain excess of the combustible gas. For example, in a stoichiometric mixture with air the content of hydrogen is 29.5 vol. %, while the maximum rate of flame propagation is observed with an H_2 content of 42 vol. %; in a stoichiometric mixture with air the methane content is 9.5 vol. %, while the maximum flame propagation rate is observed with a methane content of 10.5 vol. %, etc.

A reduction in the content of combustible gas in the mixture leads to a reduction in the quantity of heat transmitted from the

Explosive Limits of Gas-Air Mixtures

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flame front to the next layer; finally this quantity of heat becomes so small that it is no longer capable of heating the following layer to the ignition temperature. Naturally, when the content of combustible gas in the mixture reaches such a small content the flame can no longer propagate in it. The minimum content of combustible gas (in vol. %) in a gas-air mixture at which the flame still propagates in the mixture is called the *lower limit of flame propagation* in the mixture, or the *lower explosive limit* of the given combustible gas. The magnitude of the lower explosive limit differs for different gases. For hydrogen it is 4.1 vol. %. This means that any mixture of hydrogen with air in which the hydrogen content is less than 4.1 vol. % cannot explode on ignition, since flame will not propagate in it. The same is true of other combustible gases; carbon monoxide mixed with air ceases to explode when its content is less than 12.5 vol. %; methane ceases to burn at a content less than 5.3 vol. %, etc.

An increase in the content of combustible gas in a mixture leads to the same results: at first the flame propagation rate in the mixture is reduced because of the reduction in the quantity of burning gas, and then, when a certain maximum content of combustible gases in the mixture is reached - a content at which the quantity of heat being liberated becomes inadequate to heat the layer of mixture following behind the flame front to the ignition temperature - it becomes equal to zero, i.e., the flame ceases to propagate in a mixture which is this rich in combustible gas. The maximum content of a combustible gas (in vol. %) in a gas-air mixture at which a flame will still propagate is called the *upper limit of flame propagation* in the mixture, or the *upper explosive limit* of the given combustible gas. The upper explosive limit is 74 vol. % for a mixture of hydrogen with air; it is the same for a mixture of carbon monoxide with air, and for a mixture of methane with air it is 13.9 vol. %. This means that if the content of these gases in mixtures with air is greater

than the indicated values, when they are ignited flame cannot propagate in them and the mixture will not explode.

Figure 30 is a graphic presentation of the change in the flame propagation rate as a function of the content of combustible gas in a mixture; it also shows the values of the upper and lower explosive limits for the major combustible gases. The content of combustible gas in a gas-air mixture is plotted on the horizontal axis, while the flame propagation rate is plotted on the vertical axis. Projection of the beginning and end of the curve to the horizontal axis will give the upper and lower explosive limits, respectively. From the graph it is clear that at both the upper and lower explosive limits (projections of the beginning and ending of the curves to the vertical axis) the rate of flame propagation is approximately identical for all the combustible gases, comprising about 10-20 cm/s.

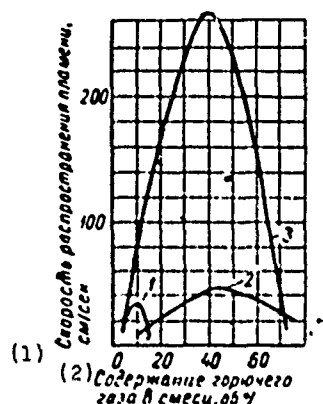


Fig. 30. Flame propagation rate as a function of the content of combustible gas in mixtures for the major combustible gases. 1 - methane-air mixture; 2 - mixture of carbon monoxide with air; 3 - hydrogen-air mixture. KEY: (1) Flame propagation rate, cm/s; (2) Content of combustible gas in mixture, vol. %.

When the combustible gas in a gas-air mixture itself consists of several combustible gases (for example, natural gas, Moscow mixed gas, etc.), the nature of the change in flame propagation rate as a function of combustible-gas content in the mixture remains the same as for simple combustible gases: its maximum magnitude occurs at a certain excess of the combustible gas, while with enrichment or leaning of the mixture it is reduced, going to zero at the upper and lower explosive limits.

For natural gas the maximum rate of flame propagation consists of 0.35 m/s; the lower explosive limit is about 5 vol. % and the upper limit is about 14 vol. %. This is to be expected, since natural gas consists basically of methane. The addition of artificial gases containing hydrogen and carbon monoxide to it will change these quantities, with the change being in direct proportion to the amount of these gases added to natural gas.

It is very important to keep in mind that different impurities can strongly alter both the flame propagation rate and the magnitude of the concentration limits. In this respect moisture and dust in gas play a major role; therefore the figures given above can serve only as tentative values.

The Phenomena of Explosion and Detonation

Calm flame propagation in a cold gas-air mixture requires that the pressure always remain constant. If a gas-air mixture is ignited in a closed vessel with more or less strong walls, the combustion products formed cannot expand freely and since their temperature is very high, this will lead to an increase in pressure throughout the entire volume of the gas-air mixture, up to magnitudes on the order of 10 at. The mixture is heated to the ignition temperature and explodes immediately over the entire volume, regardless of the flame propagation rate.

In order to understand why an increase in pressure is connected with heating of the mixture we must recall the process occurring in the Diesel cylinder. Air is sucked into the cylinder during its first stroke; on the second stroke the piston compresses it. The work expended on compression is converted into heat, and the air is heated to a temperature several hundred degrees above the ignition temperature of the fuel. Therefore, when fuel is injected into the cylinder at the end of the second piston stroke it self-ignites and burns.

A similar conversion of the work of expansion of combustion products into heat occurs when a mixture is ignited in a closed vessel. At the moment of explosion of the entire volume of gas-air mixture its mass is instantaneously converted into combustion products. Absorbing all of the heat liberated during the reaction, these products are very strongly heated and, like all gases, strive to expand. Since in a closed area this is impossible, the pressure of the combustion products grows until the walls of the enclosure cannot withstand the pressure and are destroyed. Then the gas rushes outward forcefully. A blast wave is formed, propagating in all directions and destroying surrounding objects, as well as injuring persons in the vicinity.

Example 11. We will assume that instantaneous combustion - i.e., explosion - of a stoichiometric mixture of methane with air occurs; the initial mixture temperature is 20°C , i.e., $T_1 = 273 + 20 = 293^{\circ}\text{K}$. In the first instant virtually all of the liberated heat will be expended to heat the reaction products; consequently, the temperature of the latter will be close to the theoretical combustion temperature of methane (about 2000°C), i.e., $T_2 = 273 + 2000 = 2273^{\circ}\text{K}$. Since the combustion reaction proceeds without a change in the number of kilomoles (i.e., the normal volume of reaction products is the same as the normal volume of the mixture), the explosion is accompanied by an increase in pressure. According to formula (1) (Charles' law),

$$p_2 = \frac{p_1 T_2}{T_1} = \frac{2273 p_1}{293} = 7.75 p_1.$$

Thus, if the absolute pressure of the mixture prior to explosion equaled 1 at, after the explosion the pressure of the combustion products equal 7.75 at.

From Example 11 we clearly understand the purpose of blast protection valves, which are installed in mandatory sequence in each steam boiler operating on gas fuel. Such a valve is an asbestos sheet installed in a metal frame and fastened in the wall of the boiler. Since its strength is not great, when there is an explosion inside the boiler this sheet is easily ripped away at the very instant of the explosion and provides free escape of the gases outside the boiler. As a result the pressure of the gas is not substantially elevated and the walls of the boiler retain their integrity. A similar important role is played by windows and buildings containing gas boiler units: in case of an explosion of a gas-air mixture inside the working area itself the glass will burst out under the pressure of the gases and the latter will escape from the area, leaving the walls standing. A similar role is played by doors which open outward.

During propagation of a flame over a great distance in a gas-air mixture (for example, in gas lines) the phenomenon called detonation occurs. The essence of this phenomenon is as follows. Finding it impossible to expand freely behind the flame front, the combustion products compress a layer of gas-air mixture located ahead of the flame front. A shock wave is formed; it is characterized by a high speed of travel, on the order of 1-3 km/s. In its nature the compression shock wave is similar to a sound wave: just as in the propagation of sound, there is successive compression of layers of the gas-air mixture, following one after another. The difference is that compression of air caused by a sound wave is negligibly small, while the compression of the gas-air mixture caused by a detonation wave reaches as much as 20 at. Such compression causes instantaneous heating and ignition of the mixture and therefore its combustion is propagated at the same velocity as the detonation wave itself. Naturally, a detonation is more destructive in its consequences than an explosion. Thus detonation is also propagation of a flame, but it is caused not by the thermal conductivity of the mixture, but by the displacement of a compression shock wave.

CHAPTER V

ELEMENTS OF GAS DYNAMICS AND PROCESSES OF MIXTURE FORMATION

Laminar and Turbulent Motions of Gases

The movement of a gas flow in a channel (for example, in a pipe) can be of various types. Under well-known conditions, when speed is sufficiently small and the dimensions of the channel cross section are sufficiently small, it is calm and it can be regarded as the displacement of individual, unmixing streams along trajectories corresponding to the shape of the channel. Such motion is called *laminar*. Under steady-state conditions the velocity of the gas at any point of a laminar flow is constant in time and is directed toward the motion of the flow. It differs at different points in the channel section because friction of the gas on the walls slows its motion. In this case the slowing action of the walls is transmitted from layer to layer due to internal friction (viscosity) of the gas, weakening with distance of the layer from the wall. For this reason the profile velocities in the flow cross section takes on the form shown in Fig. 31a (velocity and direction of motion of the gas are shown by arrows of different lengths - vectors). The vector of axial velocity has the greatest length, while vector length is reduced with distance from the axis of the section, becoming equal to zero at the wall itself. This means that velocity is maximum in the center of the section and is reduced to zero on the walls.

Thus if it is necessary to determine the flow rate of a gas through a pipe we must deal with a certain average velocity for the considered section. It is known that during laminar motion this average velocity comprises exactly half the axial velocity.

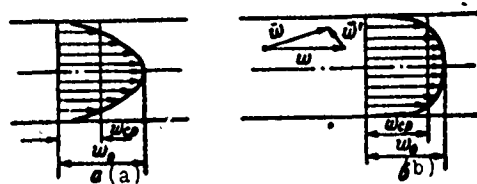


Fig. 31. Velocity profiles in different regimes of motion of a gas flow: a - laminar motion; b - turbulent motion.

Example 12. Determine the flow rate of a gas through a tube whose cross-section area is 60 cm^2 if the axial velocity of the laminar flow equals 5 m/s .

The average speed of the gas across the entire section is $5:2 = 2.5 \text{ m/s}$. Multiplying this value by the area of the tube section, expressed in square meters (in order to maintain corresponding dimensions), we will obtain the per-second flow of gas through the tube: $2.5(60)/(10000) = 0.015 \text{ m}^3/\text{s}$, which corresponds to an hourly gas flow rate of $0.015 \cdot 3600 = 54 \text{ m}^3/\text{hr}$.

Externally the laminar flow of gas is characterized by the fact that if a stream of a different, tinted gas is introduced into its flow the latter is retained for a great distance without washing out.

If the speed of the gas is increased with the channel diameter remaining the same (or if the speed is maintained with an increase in channel diameter) the nature of the gas motion finally undergoes a qualitative change. Vortexes appear in the flow; as a result the idea of independent streams of moving gas becomes meaningless.

Besides the progressive forward motion, individual elements of the gas accomplish transverse displacements; its flow becomes ever more mixed. Such motion is called *turbulent*. The speed of a gas at any point in a turbulent flow is not constant, but changes continuously both in magnitude and direction. Also under steady-state conditions of motion, when the flow rate of a gas through any flow cross section remains unchanged, the average velocity for a given point is constant in magnitude and is always directed to the same side - toward the motion of the gas flow as a whole. It could not be any other way, since in the opposite case the conditions for the steady-state regime - unchanging forward motion of the gas at a constant flow rate - would be disrupted. Therefore the instantaneous value of velocity of a turbulent flow at a given point can be presented as two velocity components of equal effect: one velocity which is constant in magnitude, directed along the flow, and is average for a given point, and one component which is variable in magnitude and direction and called pulsation velocity. This breakdown is presented graphically on Fig. 31b in the form of a velocity triangle in which the vector \bar{w} depicts the instantaneous velocity, the vector w is the constant longitudinal component, and the vector w' is the variable pulsation velocity.

The presence of a pulsation component causes intensive mass exchange and energy exchange in the radial direction; therefore the distribution of the constant longitudinal component over the cross section, shown graphically on the same figure, is vastly more uniform than during laminar motion and is characterized by the fact that the average velocity over virtually the entire section is close in magnitude to the maximum value on the axis, while close to the walls it drops sharply to zero. In this case the longitudinal velocity of the flow averaged over the entire cross section comprises from 0.75 to 0.85 of the axial velocity. Externally turbulent motion is characterized by the fact that a jet of tinted gas introduced into a transparent flow is rapidly mixed with the surrounding gas and, being diluted by it, disappears.

Pressure Losses During Motion of a Gas Flow

Movement of gas over any type of channel is possible only when there is a pressure difference between the initial and terminal sections of the channel. The fact is that any channel represents a certain resistance, and overcoming this resistance requires that the gas expend a certain amount of energy.

In the general case the total energy of 1 m³ of moving gas is made up of three components: the potential energy of pressure, numerically equal to its manometric pressure expressed in kg/m² (kg·m/m³ = kg/m²); the potential energy of position, numerically equal to the product of the height at which the gas is located above the level taken as the reading base times the specific weight of the gas (m·kg/m³ = kg/m²); and, finally, the kinetic energy of motion E_k

$$E_k = \frac{w^2}{2g} \gamma. \quad (26)$$

where w is the velocity of the gas flow in m/s; g is gravity acceleration, equal to 9.81 m/s²; γ is the specific weight, kg/m³.

Sometimes this last component is called the *dynamic head*, while the first component is called the *static head*, or the *static pressure*. As the gas moves from the initial section of the channel to the end section the sum of these three components is reduced. Difference between the initial and final values of this sum represents the loss of pressure [head].

In the simpler case when the channel lies on a single horizontal plane - i.e., there are no sloping or vertical segments - and its cross section is constant and the dynamic head consequently does not change, the pressure loss equals the difference between the static pressures of the gas in the initial and final sections of the channel. Naturally, it is measured in the same units as pressure, i.e., in kg/m² or in mm H₂O.

The resistance of the channel, which is equal in magnitude to this loss of head and is also measured in pressure units, is made up of two components: the friction drag between the gas and the walls, distributed along the entire length of the channel, and the sum of the local resistances concentrated on individual segments - turns, dampers, slide valves, changes in cross section, etc.

It is known that channel resistance is measured as proportional to the square of the gas velocity; therefore it is convenient to express it in the form of a product of some constant characteristic of the given resistance times the dynamic head $(w^2)/(2g)\gamma$. Thus, for friction drag the product of the constant friction coefficient ξ times the relative length of the tube - i.e., times the ratio of its length to diameter l/d - can serve as such a characteristic in the case of motion of a gas along a pipe of round cross section. If the shape of the channel cross section is not round (for example, if it is a rectangle), the actual diameter is replaced by its equivalent diameter, equal to the quotient from division of the square area of the channel cross section by its total perimeter: $d_{\text{эKB}} = 4F/\Pi$. The friction coefficient ξ is that fraction of the dynamic head which is lost to friction on a segment whose length equals the equivalent diameter of the channel. For smooth metal pipe ξ can be taken as equal to 0.02, while for gas lines with brick or concrete walls it is 0.04. When exact values of the drag coefficient are determined from special graphs, since its magnitude depends on a number of factors - mainly on the velocity of the gas and the smoothness of the walls.

Thus, the loss of gas head to friction along the length of a pipe in mm H_2O will be

$$\Delta h = \xi \frac{l}{d} \cdot \frac{w^2}{2g} \gamma. \quad (27)$$

Example 13. Determine the loss of head by gas to friction in a pipe with diameter $d = 100$ mm and length $l = 500$ m at gas velocity $w = 20$ m/s and a specific weight $\gamma = 0.7$ kg/m³. According to formula (27)

$$\Delta h = 0.02 \cdot \frac{500}{0.1} \cdot \frac{20^3}{2 \cdot 9.81} \cdot 0.7 = 1430 \text{ mm H}_2\text{O}$$

For local resistances the quantity called the coefficient of local resistance ζ , usually determined experimentally, is a constant characteristic. Loss of head to local resistances is determined as the product of the indicated coefficient times the dynamic head of the gas flow. Thus, this coefficient is that fraction of the dynamic head which is lost in overcoming a given local resistance. Values of coefficients of local resistance are taken from special tables.

The quadratic relationship between channel resistance and gas-flow velocity permits, in practice, the use of readings from manometers which measure gas and air pressure ahead of a burner in order to determine their flow rates. Consequently these instruments can be used to monitor and regulate the productivity of the burner and the air conditions of combustion. Actually, the pressure of the gas and the air is reduced to zero in the burner and consequently the manometer readings give the true values of the gas and air resistances of the burner. From this it follows that the flow rates of the gas and air through the burner are changed in proportion to the square root of the ratio of pressures indicated by the manometers. For example, if the gas pressure is reduced ahead of the burner from 100 to 25 mm H₂O, i.e., by four times, its flow rate is reduced by $\sqrt{4} = 2$ times. This also pertains to air; therefore in controlling the load of mixing burners to ensure a constant air regime for combustion it is necessary that the ratio between the pressures of the gas and the air ahead of the burner remain constant.

The quadratic relationship between head loss and gas-flow velocity is also used during aerodynamic calculations of steam boilers; the essence of this matter consists in determining the required magnitude of thrust. For this purpose the total resistance of the entire stack-gas tract is calculated - furnace, gas ducts, water economizer, air heater (if present), smoke damper, flue, and chimney. Then the draft created by the chimney due to the difference in specific weights of the cold outer air and the hot gasses passing through the chimney into the atmosphere is calculated. If this draw is inadequate to overcome the resistance of the entire stack-gas tract, a smoke exhaustor is installed in addition to the chimney.

Molecular and Turbulent Diffusion as Factors in Mixture Formation

The process of molecular diffusion which was considered above as one of the transport phenomena and as causing uniform distribution of the concentration of any gas within the total volume it occupies, also plays a major role in processes of mixing gases of different types, causing the formation of a mixture which is characterized at all points of the volume it occupies by identical composition. In this connection we must once again turn to consideration of the mechanism of molecular diffusion in an immobile medium and we must clarify its laws for the conditions of a moving flow.

As was already stated, any gas - even if its general mass is immobile - is actually the arena for the liveliest endless motion of molecules. Each of them travels its path in a chaotic melange of similar molecules, "occupying" always new segments of the space occupied by the gas. In terms of their motion all molecules of a gas are absolutely equal and all of them have an absolutely identical chance of turning up in a previously tagged segment of the gas volume. The motion of each molecule, taken individually,

is completely chaotic and random. Nonetheless, the sum of the chaotic motions of billions of individual molecules always leads to one and the same result - they are so uniformly distributed over the entire volume of the gas that the concentration of the latter becomes identical at all points.

This circumstance is a manifestation of the probability law for large numbers; the most probable state of the totality of molecules (in this case - uniform distribution in a volume) when the number of molecules is large is reliable. We will imagine a vessel which is divided into two parts by an impermeable partition; the two parts are filled with different gases (e.g., hydrogen and oxygen) at identical temperatures and pressures. If a small opening is made in the partition, after a certain amount of time we will find that each of the gases has penetrated into the other half of the vessel, and has done so in such a quantity that the concentration in the two halves is completely identical. Thus, the chaotic totality of aimless motions of individual molecules leads to a completely definite and always identical result: when two different gaseous media are in contact there will be mutual interpenetration of the gases contained in them.

The frequent collisions between molecules, continuously altering the direction of their motion, cause the process of molecular diffusion to be a slow one, requiring a considerable period of time for completion, although in the end it always leads to leveling of the concentrations of the different gases and to the formation of a uniform gas mixture. The diffusion process can be accelerated significantly if eddy currents are formed in contacting gases; these currents transport whole masses of molecules from one segment to another. Such currents exist in a gaseous medium which is traveling over any channel at a sufficiently high velocity. Eddy formation significantly intensifies when gaseous flows in contact, moving in parallel,

have different velocities. In this case the mutual friction on the boundary surface leads to the formation of eddies which pull gas from one medium into the other. Eddy formation is still more intensive if different gas flows intersect.

The mutual penetration of gases into one another caused by eddy formation (turbulence) and by transport into the opposite medium of whole masses of gas is called *vortex* or *turbulent* diffusion. It is easy to see that turbulent diffusion is a substantially more rapid process than molecular diffusion. For precisely this reason it is assigned a decisive role in the organization of the process of gas combustion. However, as the reader can quickly find out for himself, molecular diffusion also plays no small role in this case. A clear idea concerning this process is of special importance when we consider questions of the formation and structure of a burning gas flame.

Structure of a Laminar Jet of Pure Gas

When a gas flows out of an opening to a space filled with an immobile gaseous medium a jet arises; this is called a free or immersed jet in the case when its development occurs in a virtually unlimited space and when the immobile gaseous medium has the same physical properties - in particular the same temperature - as the outflowing gas. This case is the simplest and most easily analyzed.

We will examine the distribution of velocities in a free jet flowing out of an end opening in a round tube; we will consider that the motion of gas in the tube and, consequently, on the outlet from it is laminar (Fig. 32). In the output's section the velocity change profile of the jet is the same as that in the tube itself, i.e., it has its maximum value on the axis and is reduced to zero at the edges of the output opening. However,

as soon as the braking action of the walls disappears the peripheral layer begins to be involved in the translational motion of the neighboring moving layer; this is caused by the internal friction of the gas, i.e., by molecular transfer of energy in the direction from the center to the periphery. For the same reason (i.e., because of the mutual molecular diffusion and exchange of energy between the moving and the immobile media) the adjacent layer of the ambient medium begins to be involved in the motion of the jet; as a result the jet cross section is increased as the distance from the outlet opening increases and the entire jet as a whole takes on the form of an expanding cone. Since the energy of motion of the gas is distributed over its entire growing mass, the speed of forward motion is reduced with distance from the outlet opening. Gradually its magnitude reduces to zero and the jet fades away to nothing, being, as it were, dissolved in the ambient medium. The outer boundaries of the jet are formed by the straight lines OB and OC, originating from point O, which we will call the pole of the jet. On these boundaries the rate of forward motion equals zero. The boundaries of diffusion penetration of molecules of the external medium into the jet are also formed by straight lines AD and ED, beginning at the edges of the opening and intersecting at point D. Within the limits of these boundaries the initial velocities of the gas emerging from the nozzle are retained. The angle α_1 formed by the outer boundaries of the jet is called the expansion angle of the jet, while angle α_2 formed by the boundaries of penetration of the external medium is called the angle of contraction of the jet core. Jet cross section FG, passing through point D, is called the transition section. Ahead of this section the axial velocity of the jet w_0 remains unchanged and equal to the initial outflow velocity $w_{0 \text{ max}}$; beyond it this velocity is gradually reduced. The segment of the jet behind the transition section is called the initial segment, while the remaining portion is called the main segment.

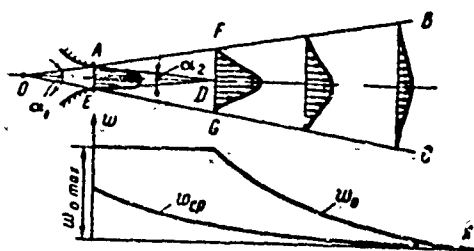


Fig. 32. Diagram of a laminar free jet.

The distribution of velocities over the cross section of a free jet within the limits of the main segment is characterized by the fact that the relative velocities at all points of any ray emerging from the pole are equal to one another. Consequently, if the distribution of velocities for any cross section is known, by drawing a series of rays from the pole it is possible to find the distribution of velocities for any other section. In the given case the term "relative velocity" is understood as the ratio of the velocity at the considered point to the axial velocity in the same cross section. Within the limits of the initial segment the parabolic law of velocity distribution is retained.

The picture of outflow is substantially complicated when the density of the medium in which outflow occurs differs from the density of the outflowing gas. In this case the jet is subject to gravitational forces, which in the end cause it to be bent. Thus, a burning jet is deflected upward (Fig. 33) in a cold medium, while a cold jet in a hot medium is bent downward. A similar bending of a horizontal jet occurs with unequal density of the outflowing gas and the immobile gaseous medium even when their temperatures are equal. If a jet is directed vertically upwards, gravitational forces alter the expansion angle of the jet and the contraction angle of its nucleus only slightly; they do not distort the velocity profile in the cross sections and they do not bend the latter. Thus if the density of the outflowing gas is less than the density of the immobile medium these angles are reduced, while in the opposite case they are increased. Therefore in moving on to consideration of mixture-formation

processes in a jet of burning gas emerging into an atmosphere of immobile air and considering that in the general case the densities of these two media are not identical, we will assume that the jet is directed vertically upwards (Fig. 34).

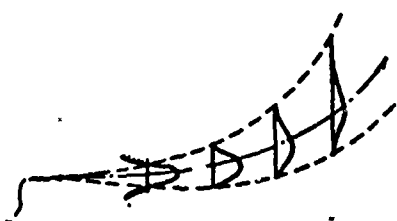


Fig. 33. Bending of a hot gas jet during outflow into a cold medium of great density.

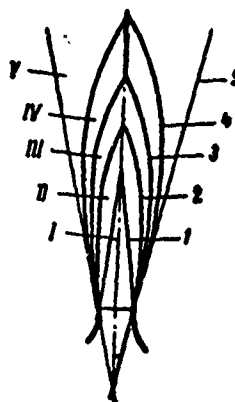


Fig. 34. Isoconcentration surfaces of a laminar gas jet.

Simultaneously with the forward motion of the gas in the axial direction, in such a jet there is mutual molecular diffusion of the gas and air in the radial direction; here the gas diffuses from the center toward the periphery, while the air diffuses from the periphery to the center. The outer boundary of the jet simultaneously is the boundary for diffusion penetration of the gas, which cannot pass beyond the limits of this boundary since it is invariably carried upward by the general forward motion of the gas. For this reason the boundary of the jet core 1 simultaneously serves as the boundary for diffusion penetration of air. Thus, pure gas is moving in the region of the core and outside the limits of the outer boundary of the jet there is quiet pure air. As regards the volume of the jet between these boundary surfaces, it contains a moving gas-air mixture, and when the jet achieves a stable state the concentration of combustible gas at each point of this volume remains constant in time.

It is obvious that each beam drawn from the pole of the jet can be characterized by a continuous reduction in the content of combustible gas from a maximum corresponding to $L_r = 100\%$ at the point where the beam intersects the boundary of the core to a zero value, $L_r = 0\%$, at a certain fairly large distance from this point. Therefore each beam contains points at which the concentration of combustible gas in the mixture corresponds to the upper ignition limit L_B , a stoichiometric content of the gas L_{CT} , and the lower ignition limit L_H . The totality of these points forms 3 smooth isocentration boundary surfaces having the form of a rounded cone with a sharp peak; surface 2, on which $L_r = L_B$; surface 3, on which $L_r = L_{CT}$; and surface 4, on which $L_r = L_H$.

Thus, as the result of molecular diffusion the stabilizing laminar flow of combustible gas is divided into a series of zones which differ from one another in principle: jet core I, which contains moving pure gas; zone II which contains a moving gas-air mixture with an excess of gas and beyond the upper limit of ignition; zone III which contains a gas-air mixture with a gas excess but which lies within the ignition limits; zone IV, which contains a gas-air mixture with an excess of air, but which is within the ignition limits; and finally zone V which contains a moving gas-air mixture which has an excess of air and which is below the lower ignition limit. If the surrounding air medium is virtually infinite, the indicated zones do not change their boundaries no matter how long the gas jet may exist.

Structure of a Turbulent Jet

The structure of a turbulent jet is, to a certain degree, similar to the structure of a laminar jet. The only essential difference is in the nature of the velocity distribution profile within the limits of the initial segment. Considering that turbulent motion is characterized by more or less uniform distribution of velocities across the section, we can consider the velocity field within the limits of the initial segment to be plane. Then

the diagram of a free turbulent jet can be depicted as shown on Fig. 35.

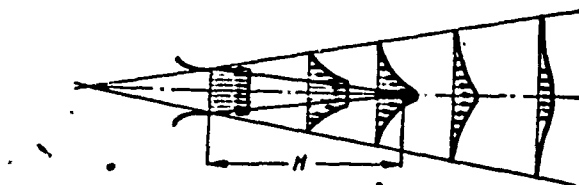


Fig. 35. Diagram of a turbulent free jet.

With increasing distance from the outlet opening, the mass of moving gas interacts with the immobile air surrounding it and picks up an ever increasing quantity of the air. The initial flat velocity profile is retained within the limits of the jet core, but beyond its limits is strongly deformed. The volume of the jet within which a rapid reduction occurs in gas velocity from the initial value w_0 to zero represents, as it were, a turbulent boundary layer whose thickness grows gradually and which at the end of the initial segment is extended over the entire cross section of the jet. The axial velocity of the gas, which is constant on the initial segment, is reduced to zero beyond it. Here the length of the initial segment, or the length of turbulent jet core H , is proportional to the diameter of the outlet opening; the ratio between them is determined by the degree of nonuniformity of the initial velocity profile.

In such a jet turbulent diffusion causes the formation of a gas-air mixture; however, during consideration of the process of mixture formation in a turbulent jet we find major significance not only in the distribution profile of the averaged concentration, but also in the instantaneous concentration field, which can be presented in the form of a system of isoconcentration surfaces, while in the plane section of a turbulent jet it can be presented in the form of a system of isoconcentration lines.

With weakly developed turbulence the isoconcentration lines, which are smooth in a laminar jet, become irregular, while at the same time remaining continuous. With strongly developed turbulence they become twisted and each of them is broken into individual surfaces which are isolated from one another (Fig. 36).

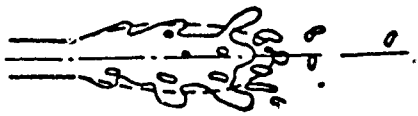


Fig. 36. Instantaneous and averaged isoconcentration surfaces in a turbulent jet.

Along with this, points with identical concentrations as averaged in time form a smooth surface, similar in shape to the isoconcentration surface of a laminar jet. Figure 36 shows such an average surface, depicted by the broken line. As is evident from the figure, individual "islands" and "peninsulas" of instantaneous concentrations are arranged on both sides of this averaged surface.

Velocity of Outflow of Gas from a Nozzle

Flow of gas occurs if the pressure ahead of the nozzle is greater than the pressure of the ambient medium into which the gas escapes. This process is accompanied by transformation of the potential energy of a gas into kinetic energy - i.e., during passage through the nozzle the pressure of the gas is reduced, so that the gas jet acquires a definite velocity.

With a given initial state of the gas its flow rate through the nozzle, like the velocity of the outflow, depends on the ratio of the pressure of the environment to pressure of the gas ahead of the nozzle. In the absence of a pressure drop, when this ratio equals unity, the flow rate of the gas equals zero.

With a reduction in this ratio (i.e., with a reduction in the pressure of the ambient medium with constant pressure of the gas ahead of the nozzle) the flow rate of the gas is increased; however, this increase goes only to a certain limit, after which it remains constant no matter how strongly the pressure of the environment is reduced.

This is explained by the fact that with a reduction in the final pressure of a gas its specific volume grows ever and ever more sharply; at the limit, during escape of the gas into absolute emptiness, the specific volume would become infinitely great. Naturally, no matter how great the area of the nozzle throughput section might be, it could not permit passage of a gas whose specific volume was infinitely great. It is therefore found that with a reduction in the pressure of the ambient medium to a certain value, called the *critical pressure*, the maximum gas flow regime is established. Further reduction in the pressure of the ambient medium does not cause a corresponding reduction in the pressure of the gas in the outlet section of the nozzle; it remains equal to the critical pressure, and accordingly the pressure drop within the limits of the nozzle is unchanged and the velocity of outflow of the gas remains unchanged. The drop in pressures between the gas leaving the nozzle and the ambient medium which arises in this case is wasted on eddy formation around the gas jet.

The ratio of the environment pressure to the pressure of the gas ahead of the nozzle is usually designated as v , while the value of v during which the mass flow rate M of the gas through the nozzle reaches a maximum - i.e., the ratio of the critical pressure to the pressure of the gas ahead of the nozzle, also called critical - is designated as v_{kp} . The magnitude of this ratio depends only on the properties of the gas itself, i.e., it has a definite value for each gas. Thus, for monoatomic gases

it equals 0.489; for diatomic gases it equals 0.528, and for three- and multiatomic gases, 0.548. From the graphic relationship shown on Fig. 37 it is clear that when $v = 1$ the mass flow rate of the gas will equal zero (i.e., there is no outflow of the gas); with a reduction in v the mass flow rate grows, reaching a maximum when $v = v_{kp}$, after which it remains constant right up to $v = 0$ (corresponding to outflow of a gas into an absolute vacuum). Accordingly, the velocity of gas outflow, equaling zero when $v = 1$, increases with a reduction in v down to $v = v_{kp}$, when it reaches its maximum value - called the *critical velocity*. With a further reduction in the pressure of the ambient medium the velocity of outflow remains constant and equal to the critical velocity. More detailed analysis indicates that the critical velocity is the velocity of sound propagation in the given gas at parameters corresponding to its state in the outlet section of the nozzle.

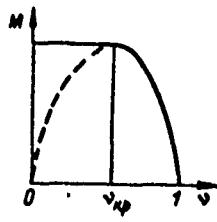


Fig. 37. Curve of gas flow rate M through a nozzle as a function of the pressure ratio v .

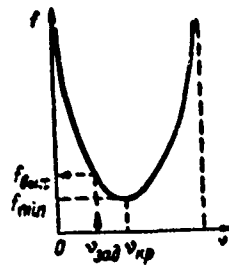


Fig. 38. Curve of nozzle working section f as a function of the ratio of pressure v with a constant gas flow rate M through the nozzle.

$$[f_{\text{вых}} = f_{\text{out}}; v_{\text{зад}} = v_{\text{given}}].$$

The above indicates that the available potential energy of a gas can be completely used in creating kinetic energy only when the pressure of the ambient medium is greater than the critical pressure, as determined in each specific case as the product of gas pressure ahead of the nozzle times the quantity v_{kp} , which is constant for the given gas. In the opposite case a portion of the available potential energy remains unused.

As was already noted, the physical explanation of the fact that a growth in the velocity of outflow occurs only in the converging portion of the nozzle and only up to a critical velocity, while in the cylindrical portion of the nozzle there is no such increase, lies in the fact that after the gas achieves critical pressure its specific volume begins to grow more rapidly than velocity grows and, consequently, a nozzle with a given cross-section area cannot allow passage of the gas which must travel through it. From this it is natural to conclude that if the nozzle is given the form of a channel which first converges and then expands, we can ensure in it a reduction in pressure even down to a magnitude below the critical. Supercritical outflow velocities can be achieved correspondingly. In order to clarify this position it is sufficient to examine the curve of required nozzle cross section f as a function of the magnitude of v , constructed on the assumption that the mass flow rate of the gas is unchanged (Fig. 38). It shows that if the nozzle is made in such a way that it first contracts and then expands, the given flow rate can be ensured even when $v < v_{kp}$ with the use of all available potential energy of the gas. For this purpose we should find on the curve the cross-section area of the outlet section of the expanding portion of the nozzle, $f_{вых}$, corresponding to the given value $v_{зад} < v_{kp}$, and the area of the narrowest nozzle section f_{min} in terms of the value of the quantity v_{kp} . A nozzle of such construction is called a Laval nozzle after its inventor, the Swedish engineer Laval.

Critical pressure is established in the narrowest section of the Laval nozzle and the gas has a critical velocity corresponding to this pressure. In the expanding portion of the nozzle there is a further reduction in gas pressure until it is comparable with the pressure of the ambient medium in the outlet section. This process is accompanied by a further growth in velocity, which in the outlet section can have a value corresponding to total use of the available potential energy of a gas.

Thus, if $v < v_{kp}$ then with a contracting nozzle the velocity of outflow will equal the critical velocity, while in expanding Laval nozzle it is greater than the critical value.

With an insignificant pressure difference, such as that which occurs during outflow of a low-pressure gas from a nozzle (to 500 mm H₂O) the expansion of the gas can be ignored. In this case the outflow picture is strongly simplified, since the velocity of the gas jet becomes proportional to the square root of the excess pressure of the gas. Thus, when natural gas (whose basic component is methane) flows out of a nozzle the approximate velocity of the gas stream in m/s will be

$$v = 4.2 \sqrt{p_r} \quad (28)$$

where p_r is the excess pressure of the gas, mm H₂O.

Comparative calculations show that the given formula yields only a small error even for a gas of medium pressure (on the order of 3000-5000 mm H₂O or 0.3-0.5 at). This is very convenient, since it makes possible rapid rough calculation to determine the required burner nozzle diameter at a given gas flow rate and, vice versa, to determine the flow rate of the gas through a nozzle of given diameter.

Operating Principle of the Gas-Jet Injector

The gas-jet injector is a very widely used device, applied during ignition of a gas to mix it with air and to inject the gas-air mixture. This, like the actual formation of the mixture, is accomplished due to the energy of the gas jet flowing out of the gas line into the burner. In simplest form the gas injector consists of nozzle 1, confusor 2, and mixer 3 (Fig. 39). The potential energy (static head) of the gas entering the injector

from the gas line is converted during passage through the nozzle into kinetic energy (dynamic head), since during passage through the nozzle its pressure is reduced and is equated to the pressure in the mixer. Because of this the gas jet emerges from the nozzle at high velocity and, pulling air along with it, creates rarefaction in the mixer. Thus, in section I the pressure is less than atmospheric. Due to the thus-created difference in pressures in the injector air is pulled from the surrounding medium, with its flow being directed by the confusor. A gas-air mixture is formed in the injector and leaves it through section II.

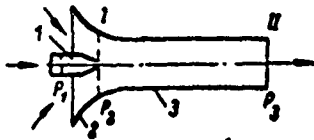


Fig. 39. Diagram of the simplest gas injector.

Analysis of the process occurring in the injector shows that the ratio of the volume flow rate of injected air to the volume flow rate of enjecting gas, called the *injection coefficient*, depends only on the ratio between the diameters of the nozzle and the mixer, the density of the gas with respect to air, and the hydraulic perfection of the mixer.

A circumstance which is extremely interesting and very valuable from a practical point of view is the fact that the initial pressure of gas is not among the enumerated factors. This means that during all changes in the flow rate of the gas the injection coefficient remains unchanged. It should be noted that this theoretical conclusion is confirmed in practice over a fairly broad range of changes in the flow rate of gas through the nozzle.

Turbulent Mixing of Gas and Air in Burners

The injector is a good mixing device, ensuring the obtaining of virtually uniform gas-air mixtures, but the great length

of the mixing segment limits its application in those cases when the question is one of mixing large quantities of gas and air. Besides this, their total mixing up to the moment of exit into the furnace is not always necessary or desirable. Along with this, the application of fan blasting opens the possibility of intensive mixing of gas with air in large quantities through the action of turbulent diffusion arising when the gas and air flows encounter and mutually penetrate one another.

In the simplest case flows of gas and air collide at an angle (Fig. 40). It is easy to see that in this mixing occurs not only because of turbulent transfer of finite volumes from one flow into the other, but also due to the kinetic energy of the forward motion of the flows themselves. This circumstance is of primary significance because during ignition of high-calorie gases the quantity of air is many times greater than the quantity of the gas itself and the possibility of imparting to the air a sufficiently great amount of energy in the fan makes it possible to shorten the required mixer-segment length considerably (as compared with mixers of the injection type, in which the process is due to the energy of the gas alone).

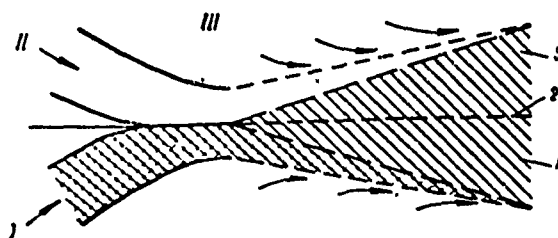


Fig. 40. Mixing of flows at an angle to one another.
 I - jet of air; II - jet of gas; III - environmental air. 1 - mixture of air with combustion products;
 2 - combustion surface; 3 - mixture of gas with combustion products.

4

In calculating the indicated ratio between the quantities of air and gas, the gas is usually introduced into the airflow in the form of a large quantity of individual jets directed at an angle to its axis. In this case the flow of gas can be central - in a radial direction from the axis of the flow to its periphery - or peripheral, in the direction from the periphery of the flow to its axis. In these cases the basic problem is the distribution of the gas in the section of the airflow, which must be such that at all points of the airflow, the ratio between the quantities of gas and of air will be as nearly as possible the same as on the average over the entire cross section - i.e., such that this distribution will be uniform. The most perfect solution of this problem is differentiation of the gas supply through openings of different diameters.

Figure 41 shows a diagram of the development of an individual jet of gas in a transverse flow of air. The flow of air deflects the gas jet from the initial direction and it is twisted, finally taking the direction of the airflow itself. The depth of penetration of the jet is characterized by the ratio of the distance h to the diameter of the outlet opening d_0 (which is equal to the initial diameter of the jet). Studies have shown that this quantity depends on the angle of attack α and also on the ratio between the velocities of the gas and the air, as well as their densities. With outflow of gas into a stream of air from openings of different diameters at identical velocities and angles of attack, the depth of penetration of the jet is proportional to the diameter of the outlet opening. This circumstance permits using the appropriate arrangement of outlet openings to ensure uniform distribution of gas in an airflow.

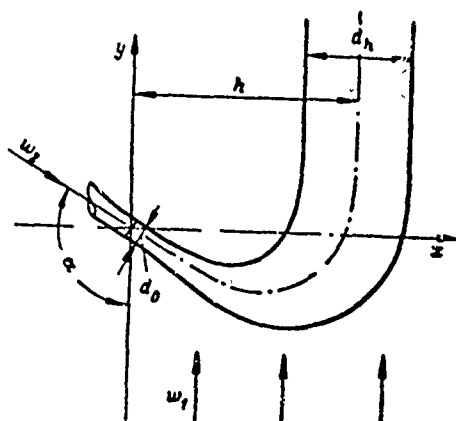


Fig. 41. Diagram of the development of a gas jet in an airflow.

To intensify the mixing processes it is sometimes advisable to use preliminary twisting of the airflow by means of blade swirlers or its tangential introduction into the air channel. Blades for devices of the first type can be flat or shaped, with a helical working surface in the last case. Tangential supply can be simple (Fig. 42a) or conical (Fig. 42b). The twisted flow has a number of specific features as compared with a straight flow. The angle of expansion of the flow at the outlet from the swirling device is larger, corresponding to its shorter bend length. Besides this, it has a very high injection capacity; because of this, the correct selection of the twist angle makes it possible to obtain a reverse flow in the axial region of the current. This opens broad possibilities for controlling the intensity of mixing through the organization of additional supply of air into the axial region of the flow and by changing the quantity of this additional air.

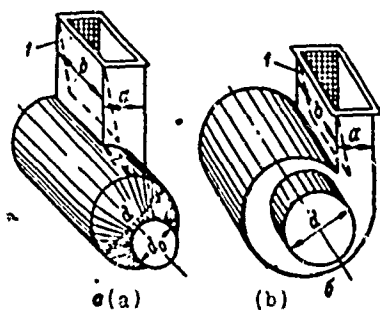


Fig. 42. Diagram of a simple tangential (a) and helical (b) supply of air.

1 - tongue gate.

The flow aerodynamics during tangential supply and also the resistance of the swirler depend mainly on the ratio of the areas of the cross sections of the fitting ($a \times b$), the chamber in which swirling occurs ($\pi \frac{d^2}{4}$), and the outlet cross section of this chamber ($\pi \frac{d_0^2}{4}$). It has been established by experiments that the swirling in the cavity of a tangential feed is the greater, the smaller the ratio of the first area to the second. Correspondingly the divergence angle of the flow is increased and its range of effect is reduced. When the ratio between these areas remains unchanged the swirling of the flow is increased with a reduction in the ratio a/b with simple tangential feed and reduced during helical tangential supply.

In addition to these possibilities for selecting the required angle for swirling of the flow, during development of the design of a mixer it is possible to vary it during the operating process by means of a gate of the tongue type, 1 (see Fig. 42). Narrowing the tongue-type gate causes an increase in twisting of the airflow.

CHAPTER VI

DIFFUSION COMBUSTION OF GASES

Plane Structure During Burning of a Laminar Gas Jet

As was shown earlier, when a jet of combustible gas flows into an atmosphere of immobile air a gas-air mixture is formed and the jet takes on the structure depicted on Fig. 34. If such a jet is lighted the gas-air mixture ignites and the flame propagates rapidly throughout the entire volume included between boundary isoconcentration surfaces 2 and 4. For practical purposes this appears to be a flare, encompassing the entire indicated volume and lasting only a thousandths of a second. After an instant zone III, which contained a mixture with an oxygen deficiency, no longer has a single molecule of the latter and combustion ceases. In exactly the same way zone IV, in which there was a mixture with an oxygen excess, no longer contains a single molecule of combustible gas and combustion also terminates. The single place in which molecules of combustible gas (diffusing from the jet or carried there by its general motion) and molecules of oxygen (diffusing from the surrounding air into the jet) meet is surface 3, with a stoichiometric ratio, on which the combustion process is fixed. A thin (a few tenths or even thousandths of a millimeter thick, depending on the properties of the combustible gas) glowing layer of hot stoichiometric mixture, called the flame envelope, is formed on this surface.

As a result the entire structure of the jet is changed (Fig. 43). Instead of three boundary surfaces, only flame envelope 1 remains. Zone 2, filled with a flow of combustible gas, will be enclosed inside this flame envelope; as it leaves the nozzle, the flow is uniformly distributed over the entire flame shell and burns in it. Molecules of the products formed during combustion - carbon dioxide and water vapor - diffuse in the opposite direction, i.e., from the flame shell into the depth of the gas flow. The reverse flow of the gas throws them back into the flame shell and allows them to penetrate very deeply into the depth of the flow; nonetheless, the region of zone 2 which is adjacent to the flame envelope is filled with a mixture of combustible gas and combustion products, with the concentration of the latter diminishing in the direction of the nozzle opening and gradually vanishing.

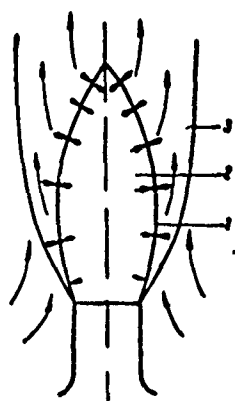


Fig. 43. Structure of a laminar diffusion flame.

On the outside the flame envelope is surrounded by zone 3, into which the entire mass of combustion products being formed will finally penetrate. Very high in temperature and, consequently, of low density, the flow of combustion products tends to rise upward and form convective currents in the immobile mass of air surrounding it. In the main these currents facilitate the supply of the oxygen required for combustion to the flame envelope. However, convection alone (i.e., displacement of gaseous masses under the action of density differences) would not be sufficient

to maintain the combustion process in the flame envelope. Surrounded by a flow of combustion products and penetrating into zone 3, fresh air would pass along the flame shell without participating in the combustion process. The fact is that the continuous consumption of oxygen molecules in the flame envelope creates a situation of constant deficiency of such molecules in its immediate vicinity. The concentration of oxygen here is always much less than in a surrounding medium and therefore the gradient of concentration directed toward the flame envelope is of great magnitude. For this very reason a diffusion flow of oxygen arises, directed from all sides toward the outer surface of the flame envelope.

Combustion has a similar character in those cases when a laminar gas flow is surrounded by a flow of air moving parallel to it and at the same velocity, or when a flow of gas and a flow of air move in a closed channel parallel to one another and at equal velocity. In all these cases the basic process which supports combustion in a flame envelope is molecular diffusion; therefore the entire combustion process as a whole is called *diffusion burning*, while the flame itself, which separates the flow of combustible gas and that of air, is called a *diffusion flame*.

Nature of the Luminescence of a Laminar Flame

The intraflame zone (Fig. 43), which can be called the core of a laminar flame, and especially that segment of it located closest to the inner surface of the flame shell represents the point where molecules of combustible gas encounter molecules of the combustion products which penetrate from the flame envelope. Since they carry a large reserve of kinetic energy, during collision with molecules of combustible gas the molecules of combustion products transfer part of their energy to the gas molecules and increase the velocity of their chaotic motion.

Simply stated, this means that the combustible gas which is mixed in the flame core region with hot combustion products is heated as it approaches the flame envelope.

During this preheating different combustible gases behave differently, depending on whether they are heat-stable or heat-unstable. Molecules of heat-stable gases (including hydrogen and carbon monoxide) are not changed during heating, and the only thing which occurs is that the temperature of these gases is raised. The situation is entirely different with the heat-unstable gases (including methane and other hydrocarbons). When the temperature is raised sufficiently high without access of air they begin to decompose and form other chemical substances. For example, methane begins to break down into atomic carbon and hydrogen at temperatures as low as 300°C , with this decomposition being more complete, the higher the temperature. Thus at 500°C about half of the methane is completely decomposed; at 750°C the quantity is about 90%, and at 900°C this decomposition of methane is virtually complete. Approximately the same picture is observed during heating of other hydrocarbons in the absence of oxygen; in all cases atomic carbon is formed.

The process of heating of a combustible gas by combustion products in the core of a diffusion flame will accordingly develop differently as a function of the nature of the gas being heated. If the combustible gas consists of heat-stable components, hydrogen and carbon monoxide (for example, water producer gas), no chemical changes occur in this zone. Therefore the inner portion of the diffusion flame remains transparent and the flame as a whole, although it has an azure color due to the luminescence of the flame envelope, is basically transparent.

A different picture is observed when the combustible portion of a gas consists of thermally unstable components (e.g., natural or mixed gas). In this case extremely fine particles of solid material

appear in the region of the core; these are formed by agglomeration (uniting) of individual carbon atoms. The dimensions of particles of this material (soot) are extremely small, comprising only a few tenths of a micron ($0.3-0.4 \mu\text{m}$). However they appear in extremely great quantities and when they ignite they impart to the flame a relatively bright light-yellow color, characteristic for diffusion combustion of hydrocarbon gaseous fuel. The presence of incandescent solid particles of carbon causes the high intensity of the flame; in a number of cases this is of great practical significance, since it permits direct organization of intensive radiant heat exchange inside the furnace.

Properties of the Transition of Laminar Combustion Into Turbulent Combustion

With an increase in the gas flow rate its axial velocity inside the flame envelope is increased, and since the rate of diffusion of oxygen into the flame remains unchanged the process of mixing is, as it were, shifted along the axis of the jet in the direction of its motion. Because of this the flame envelope is fixed in space somewhat further from the nozzle, with the distance increasing with an increase in the flow rate of the burning gas; the length of the flame is increased, which agrees fully with the fact that a greater quantity of gas begins to burn in the flame envelope per unit time and consequently the surface of the flame envelope must be increased.

However, this property is observed only so long as the motion of the gas remains laminar. When its velocity grows to a certain critical value the laminar motion of the gas begins to convert into turbular motion. The tip of the flame becomes unstable and begins to pulsate. With a further growth in the velocity of the gas this instability progresses and a noisy "turbulent brush" of flame appears; this begins at the height of breakaway of the flame

envelope at that point where the laminar regime of gas motion is disrupted and turbulence develops. In the zone of turbulence a qualitative change occurs in the nature of diffusion and consequently in the actual process of combustion itself. Diffusion ceases to be molecular and becomes turbulent. The swirls which arise inside the jet are transferred to the zone surrounding the flame envelope and, seizing oxygen from this zone, they carry it to the flame envelope in a significantly greater quantity than is possible during molecular diffusion. This causes the formation of a turbulent brush, since the flame envelope (which was smooth during laminar motion of the gas) becomes uneven and ragged, and then breaks up into individual combustion sites surrounded both by unburned gas and by unreacted oxygen. This entire mass is displaced chaotically with the formed combustion products.

Naturally, with such a change the ignition surface is sharply increased and therefore the combustion process is converted to another and higher level of intensity. The total length of the flame is significantly shortened, but at the same time combustion loses its quiet character, the flame becomes uneven, and at very high outlet gas velocities the flame separates from the outlet opening of the nozzle and may even be detached entirely.

Figure 44 gives a very clear picture of the change in the nature of a diffusion flame; this figure illustrates the results of experiments on the ignition of city gas during various outflow velocities from a pipe 3.1 mm in diameter into an atmosphere of immobile air. Nine open flames are shown on the diagram; the three left flames are laminar, the three middle flames are transition flames, and the three on the right are turbulent flames.

The region of laminar conditions, as is clear from the figure, is characterized by a sharply marked flame contour, unchanging flame shape, and an essential increase in the length of the flame with an increase in gas velocity.

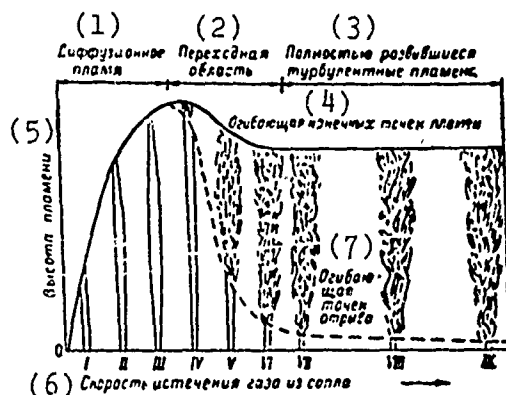


Fig. 44. Change in flame length and combustion conditions with an increase in the velocity of the gas jet.

KEY: (1) Diffusion flame; (2) Transition region; (3) Completely developed turbulent flames; (4) Envelope of flame and points; (5) Flame height; (6) Velocity of gas flow from the nozzle; (7) Envelope of detachment points.

The region of transition conditions is characterized by the appearance of turbulence in the tail (upper) portion of the flame and its gradual spreading both into the depth of the flame and into the counter gas flow toward the root of the flame. Due to the increase in the intensive combustion the flame length is not increased in the transition zone as the gas velocity increases; quite the reverse, it is reduced. Here the upper, turbulent segment is elongated and the lower, laminar segment is shortened.

The region of turbulent conditions is characterized by the fact that the point of breakaway of the flame envelope approaches almost up to the nozzle; a further increase in velocity of the gas has virtually no influence on the total length of the flame nor on the position of this breakaway point. The specific interference which appears when turbulence arises grows with an increase in turbulence. An increase in turbulence leads also to intensification of mass exchange between the gas jet and the surrounding air; as a result the inner region of the torch is continually more aerated and, where the torch was opaque and yellow during the laminar regime, as turbulization of the flame progresses it gradually becomes azure and transparent. Its luminescence weakens accordingly.

It should be noted that the reduction in flame length in the region of transition conditions and its constant length in the

region of turbulent conditions will be characteristic only for small-diameter burners. Determination of the length of a free diffusion flame during ignition of generator gas in burners of different diameters shows that this regularity is disrupted with transition to larger burners. Such burners are characterized by a continuous growth in length of the flame not only in the region of laminar conditions, but also in the transition and turbulent regions. This is shown clearly on Fig. 45, which presents the results of the study mentioned above.

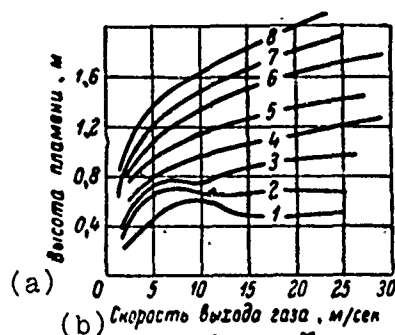


Fig. 45. Change in the length of a vertical flame as a function of the velocity of gas flow and the diameter of the burner (d).

d, mm; 1 - 10.1; 2 - 15.2; 3 - 20.3; 4 - 25.1; 5 - 30.2; 6 - 35.3; 7 - 40.2; 8 - 45.3.

KEY: (a) Flame height, m; (b) Velocity of gas escape, m/s.

From this figure it is clear that the height of a completely turbulized flame grows almost in proportion to the diameter of the nozzle. This is completely to be expected, since a similar relationship occurs between the geometric dimensions of jets of different diameter in the absence of combustion. Simultaneously gas analysis shows that the height of the visible front of turbulent diffusion of a flame exceeds by more than 50% the height of the surface of the stoichiometric ratio. This is due to the difference in the structure of the mixing surface for turbulent and laminar jets. While the isoconcentration surface of a stoichiometric ratio is continuous and has a regular form for a laminar jet, the corresponding surface of a turbulent jet (as shown in Chapter V (Fig. 36)) is at any given instant a complex totality of isolated irregular, twisted surfaces of different size and shape. Since the flame is formed on precisely these surfaces, it has a complex form and pulsating configurations.

The radiation from such a diffusion flame is so intensive that to the naked eye its surface appears to be an outer boundary of that volume in which islands of flame are located, however briefly. The outer visible boundary corresponds to the surface on which the degree of combustion is approximately equal to 99% (determined by analysis of samples taken after a finite time interval).

A substantial increase in the velocity of gas outflow can lead to breakaway of the flame from the nozzle orifice. In this case it either "rises" above the nozzle by a certain distance or it is completely carried away by the gas flow and is extinguished. In this connection we distinguish between the concepts of partial and complete breakaway of the flame. The velocity of the gas at which breakaway of the diffusion flame occurs is, as a rule, extremely high and depends not only on the properties of the gas itself but also on the dimensions of the nozzle. Besides this, it depends on aerodynamic and thermal factors and can be substantially increased by the use of various types of stabilizing devices.

Turbulent Gas Torch

Turbulization of a flame, the consequence of an increased gas outflow velocity into an immobile air medium, can be characterized as unique and spontaneous and as the consequence of a change in the actual conditions of motion of the gas flow. The intensification of mixing processes which is connected with it brings to mind the possibility of still deeper intensification of both the mixture-formation process and of the entire process of diffusion combustion by additional artificial turbulization of the flow. This idea has been widely realized in engineering through the use of various types of mixers, which make it possible to improve the mutual penetration of the gas and air flows. As was already pointed out, the measures directed toward achievement of

the given goal include organization of intersecting flows of gas and air, twisting of the air flow by means of guide vanes, separation of the gas flow into a number of individual jets of small diameter which penetrate the air flow at an angle, etc.

In all these cases we are also dealing with diffusion, both molecular diffusion (as during the combustion of a laminar gas jet) and with turbulent diffusion. With artificially organized turbulence of the gas and air flows, as also with sufficiently developed natural turbulence of an open gas flame, the idea of a flame envelope and of those zones with which we dealt during consideration of laminar diffusion flames will lose its meaning. In place of all this, a diffusion torch arises in the region of mixing of flows of a combustible gas and air; throughout the entire volume of this torch there will occur, simultaneously and with greater or lesser degrees of intensity, both mixing of the gas with air and heating of both — both separately and in the mixture due to heating by combustion products — and finally the actual chemical reaction of combustion. The shape and length of such a torch, and equally the arrangement of the regions of greatest intensity of individual process elements, will be determined as a whole by the direction and nature of the motion of gas and air flows. For example, if the air flow emerges into the furnace space in parallel to the longitudinal axis of a torch which is twisted little or not at all, while the gas jet intersects this flow at an angle forming a converging cone (as in annular burners), a long, narrow torch is obtained. With strong twisting of the air flow, as for example by the rotation of guide blades, mixing quality is improved and the torch is shortened, but is more or less noticeably broadened.

Various forms of control and forcing of turbulent diffusion processes were examined above. Here we may only point out that since the combustion rate is always determined to a significant

degree by the rate at which gas is mixed with air, these methods simultaneously are a means for controlling and forcing the entire combustion process as a whole.

The individual stages of the combustion process in a turbulent diffusion torch are not concentrated in definite narrowly marked zones, as in a laminar flame, but are more or less scattered throughout the entire volume of the torch. This also relates to the process of thermal dissociation of the combustible gas; this occurs (when thermally unstable components are present) in those elements of the volume in which at any given moment the gas encounters combustion products in the absence of oxygen. The finely dispersed solid carbon particles which are formed in these elements find themselves immediately afterwards in the vicinity of oxygen molecules, and therefore the process of burning of these solid particles is developed throughout the entire volume of the turbulent torch. This combustion is a reaction between substances in different phases — solid and gaseous. Therefore it occurs not in the volume but on the surface of individual particles, which gives rise to a number of specific features.

The combustion of carbon particles can be broken down schematically into several successive stages. The first of these is the arrival of oxygen by diffusion from the surrounding gaseous atmosphere to the combustion surface. Since they are finely dispersed, these particles take part in all of the movements of the gaseous medium surrounding them — i.e., they remain motionless with respect to it. Therefore, despite the turbulent nature of the torch as a whole, only molecular diffusion plays a role in the supply of oxygen to their surface, while turbulent diffusion is completely excluded.

The second stage is the chemical adsorption of oxygen molecules; this develops under the influence of the force field

which is created by carbon atoms on the surface of the particles. The concluding stage of combustion of carbon particles involves the entering into the reaction of the oxygen molecules adsorbed on the surface; this results in the formation of carbon monoxide and dioxide, which leave the surface in the gaseous state. Subsequently carbon monoxide contacts oxygen and burns, also being converted into carbon dioxide.

The resulting rate of interaction of the solid and gaseous stages is determined by which particular one of the considered stages (diffusion of oxygen, its chemical adsorption, or the reaction itself) is limiting - i.e., which one proceeds slowest. If diffusion is slower then it is said that the process occurs in the diffusion region; if the chemical reaction is slower, it is said that the process occurs in the kinetic region.

Naturally, in the high-temperature portion of the torch the combustion of solid carbon particles occurs in the diffusion region. If we consider that penetration of oxygen molecules into it occurs only due to molecular diffusion, with complete absence of turbulent diffusion, it is possible to assert that this process is the "narrowest" place in the entire flame process as a whole. At the same time, it is fully probable and possible that carbon particles cannot burn in the high-temperature region of the torch and will be carried beyond its limits by the displacement of the surrounding gaseous medium. In such a case their combustion transfers from the diffusion region to the kinetic region and then in general is terminated. As a result black tongues consisting of unburned and cooled carbon particles are formed in the low-temperature tail portion of the flame. Uniting into flakes and being deposited on heating surfaces and walls of gas ducts which they encounter, they form the deposit known as soot.

CHAPTER VII

COMBUSTION OF A GAS-AIR MIXTURE

Flame Structure with Partial Premixing of the Gas with Air

We will assume that a tube similar in its construction to that considered in the preceding chapter releases not a pure gas but a preliminarily prepared gas-air mixture which contains an excess of combustible gas, but which still lies within the ignition limits. We will also assume that the outflow velocity of the gas-air jet is small and that its motion is laminar. When such a jet is ignited a flame is formed whose structure differs in principle from that of the laminar diffusion flame examined above.

The difference consists in the fact that the ignition and partial burning of the gas issuing from the tube does not in this case require the diffusion of oxygen from the surrounding air. Oxygen is included in the gas-air mixture composition. Therefore immediately after ignition a flame not only arises at the outlet of the mixture of the tube, but it also tends to penetrate into the tube itself, moving in this direction at the normal rate of propagation of a flame, which we already know. However, if the rate of outflow is sufficiently great no penetration of the flame inside the tube will occur; the reason for this is fully understandable - it is pushed back by the counterflow of the gas-air mixture.

A swimmer who attempts to move up a river against the current will be successful only if his speed of motion exceeds the speed of the counterflow of the river. In the opposite case, despite all his efforts, he will be carried backward by the current and will stop losing ground only where, for some reason, the speed of the current is reduced and becomes equal to the swimmer's rate of travel. By complete analogy with this, the combustion zone is stabilized in that region where the rate of outflow of the mixture is reduced to such an extent that it becomes equal to the normal rate of flame propagation. It should also be considered that a flame tends to penetrate inside the tube not only in the axial direction, but from all sides, selecting the path of least resistance. Therefore, in studying the given process it is necessary to take into account not the velocity of motion of the jet parallel to its axis, but the component of this velocity which is directed precisely counter to the motion of the flame.

In order to clarify the principles for breaking down velocity into its components, it is again appropriate to turn to the example of the swimmer. In what direction should he swim in order to cross a river (Fig. 46), if the speed which he can achieve and also the rate of flow of the river are known (depicted on the figure in a determined scale by segments 1 and 2)? It is obvious that to accomplish this he must swim at an angle to the current and his efforts must be calculated so that component 3 of his velocity, directed against the current, will precisely equal the speed of the latter. Then he will not be carried off by the current and will cross the river at the vector shown by segment 4 on the figure. Now it becomes clear that a flame front which is attempting to penetrate inside a tube must be stabilized at those points at which the component of the speed of forward motion of the motion directed against the flame is equal in magnitude to the flame propagation rate. The totality of points which satisfy this condition form a surface having the appearance of a rounded cone (Fig. 47). At any point on this cone the rate of forward motion

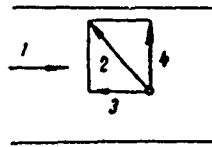


Fig. 46. Diagram of analysis of velocities of a swimmer crossing a river.

of the mixture can be broken down into two components - the normal to its surface and the tangent to it. The normal component is equal in magnitude to the flame propagation rate in the given mixture and therefore is compensated. The tangential component is not compensated by anything and therefore the elementary annular layer of burning mixture is "carried" along the surface of the cone toward its apex, being replaced by a neighboring elementary burning layer which is carried downward. There is, as it were, a continuous ignition of the upper elements of the burning surface by the lower elements. This explains the continuity and unique form of the surface of the flame front. However, this cannot explain the stability of the flame front, retained in a fairly broad range of mixture outflow velocities, since it is unclear just what factor ignites the very lowest elements of the burning surface.

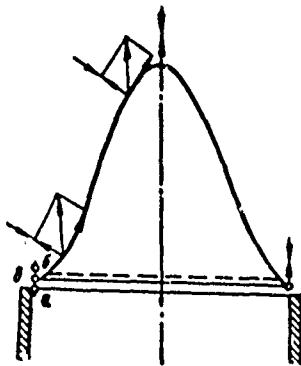


Fig. 47. Conical combustion surface of a gas-air mixture.

[$a = a$; $b = b$; $c = c$]

The answer to this question can be found on the basis of the following reasoning. As was shown above, the speed of the mixture in the tube is not identical across its section: it drops with approach of the mixture to the walls and immediately at the

wall this velocity equals zero. Therefore the flame would inevitably penetrate inside the tube if the walls did not cool the mixture and prevent the propagation of flame in it. For practical purposes, even at that distance from the wall (in the direction toward the center of the cross section) at which the mixture velocity has a sufficiently great value (less, however, than the normal velocity of flame propagation) the flame cannot propagate in the direction counter to the flow of the jet of mixture because at this point (point a on Fig. 47) its velocity is low and is less than the velocity of the mixture, due to the cooling influence of the wall. At the tube outlet the velocity of the mixture retains its value at a distance which is greater than that at which heat transfer through the wall continues to have an influence. Therefore at that distance from the tube end at which the velocity of the mixture changes but little the flame propagation grows to normal (point b). It is clear that a point c exists on segment a-b and at point c the flame propagation rate is precisely equal to the velocity of the mixture. At this point it is directed counter to the jet and parallel to its axis; therefore direct compensation of the velocity of mixture outflow occurs in it and the flame will have a stationary location. Around the entire periphery of the tube such points form a ring which encircles and ignites the gas jet emerging from the tube. This igniting ring acts as the stabilizer for all burning of the jet as a whole.

The deviation from normal in the flame propagation rate in the region of the igniting ring is not great and, additionally, it occurs only in a comparatively narrow zone directly adjacent to this ring (on Fig. 47a this zone is bounded by the broken lines). Therefore this deviation can be ignored and we can consider that the speed at which the mixture passes through the flame front (in the direction normal to its surface) is constant and equal to the normal flame propagation rate over the entire surface of the cone.

This premise forms a basis for the method of experimental determination of the normal rate of flame propagation called the dynamic [method]. The essence of the dynamic method lies in the fact that the unknown velocity is determined as the quotient of division of the mixture flow rate through the tube by the area of the cone surface. The latter is determined as the surface of a body of revolution whose generatrix corresponds to the profile of the flame front. This profile can be established by projecting the combustion cone in magnified form on the screen or by photographing it.

The zone of primary combustion - combustion due to the oxygen contained in the gas-air mixture itself - is an extremely thin layer of conical form and azure-blue color; in this zone a direct chemical reaction occurs, representing, as it were, a reliable filter which prevents passage of any gases from outside into the jet (we will recall that the actual process of flame propagation is the result of diffusion of hot combustion products in the direction of still unreacted cold gas-air mixture; and therefore the velocity of diffusion from without and the rate of heat propagation cannot be greater than the velocity of the flame front itself). Therefore a laminar flow of cold and pure (in the sense that it is not mixed with foreign gases) gas-air mixture travels in the region located close to the outlet opening of the tube and bounded by the cone of the primary flame.

In crossing the zone of primary combustion the mixture loses its oxygen and is converted into a mixture of combustible gas with products of complete and incomplete combustion. This mixture already has a high temperature; its volume grows substantially as compared with the initial value and therefore its motion cannot remain laminar outside the cone of primary combustion. Intensive swirling arises in the flow of this mixture; this swirling facilitates diffusion of oxygen from the ambient medium. As a result the process of secondary, diffusion combustion arises in a zone

located above the blue cone of primary combustion. From the outside the boundaries of this zone do not have a clear outline; they are, as it were, "blurred" by turbulence, but nonetheless they are noticeable and the secondary flame has a definite shape.

Thus, on the whole the flame which appears during combustion of a laminar gas-air jet has the structure depicted schematically on Fig. 48. When the content of air in the initial mixture is sufficiently high, combustion in the blue cone is accompanied by preliminary gasification of the hot gas due to the initial air; this prevents the formation of particulate carbon even during burning of natural or other hydrocarbon gases. Therefore a diffusion flame is azure and transparent. In the case when the content of carbon in the primary mixture is small the process of pyrolysis occurs in the flame; this is accompanied by the formation of particulate carbon, which results in a flame of a characteristic straw-yellow color which becomes luminescent, as in the case of purely diffusion combustion of gas.

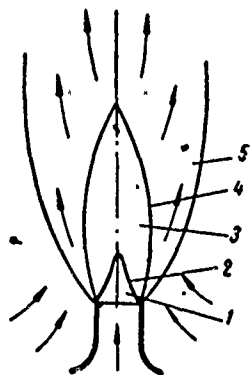


Fig. 48. Structure of the flame during combustion of a laminar gas-air jet. 1 - zone of motion of cold gas-air mixture; 2 - azure cone of primary combustion; 3 - zone of thermal decomposition of the gas; 4 - secondary combustion flame envelope; 5 - flow of combustion products.

The minimum content of primary air at which pyrolysis processes are replaced by gasification processes is

$$\alpha \geq \frac{1n}{2\left(n + \frac{m}{4}\right)}, \quad (29)$$

where k is a coefficient dependent on the thickness of the jet ($k = 1-1.4$); n is the number of hydrocarbons; and m is the number of hydrogen atoms in a molecule of the gas.

Taking the average value $k = 1.2$, we obtain a value for the content of primary air in a mixture with methane which will ensure obtaining an azure flame with no particulate carbon: $\alpha = \frac{12.1}{2(1+\frac{4}{4})} = 0.3$.

This means that if the primary mixture contains more than 30% of the theoretically required air its combustion will proceed without the formation of particulate carbon and the flame will be azure and transparent; in the opposite case the flame will be yellow and opaque.

Flame Stability During Combustion of a Gas-Air Mixture

Under "flame stability" we understand the ability of a flame to retain its normal position close to the outlet opening during minor changes in the velocity of the burning jet. Flame stability is intimately connected with the composition of the gas-air mixture and therefore we will first examine the case described in the preceding section (the mixture contained air in a quantity of 50-60% of the theoretically required amount). We are already familiar with the nature and structure of the flame which arises during combustion of a laminar jet of the given mixture: near the outlet opening in the tube an azure cone of primary combustion is formed; a secondary diffusion flame arises above it. We will begin to increase the gas-air mixture outflow velocity, leaving its composition unchanged. In this case, as one would expect, the primary combustion cone begins to be elongated, since the point at which the axial velocity of the gas-air mixture is equal in magnitude to the counterflow velocity of flame propagation and the point at which, consequently, the peak of this cone is located is shifted upward, in the direction of motion of the gas-air jet.

The total surface of the cone is increased, with the increase precisely corresponding to the increase in the quantity of gas burning on this surface. The depth of the diffusion flame is also increased and therefore the quantity of unburned gas passing along the zone of primary combustion also grows. However, in this case the flame does not lose stability.

With a further increase in the mixture's flow velocity its motion converts from the laminar regime to the turbulent. In this case the regularity of the shape of the primary flame cone is disrupted; it is elongated and blown out at the end. Nonetheless its surface continues to remain smooth. With a very high outlet velocity of the mixture and strongly developed turbulence it should be separated into individual combustion sites, but up to this point this does not occur, since combustion generally remains unstable and the flame is broken away from the outlet opening in the tube and extinguished before swirling of the jet destroys the front of the primary flame.

We will move now in the opposite direction. Beginning with the previous velocity of the outlet mixture from the tube, we will gradually reduce it. Naturally, in this case the primary combustion cone will be shortened and broadened. The diffusion flame will also be shortened. Finally, when the velocity of forward motion of the jet is reduced to such a degree that the condition of equality of velocities cannot be met the stability of combustion is disrupted and the phenomenon of breakthrough of the flame into the tube interior occurs.

From this it follows that when a gas-air mixture containing 50-60% of the theoretically required amount of air is burned the flame is distinguished by stability, but it retains stability only within certain limits. There is a minimum permissible velocity of the mixture below which penetration of the flame inside the

tube (or burner) will occur, and there is a maximum permissible velocity which, if exceeded, leads to breakaway and extinguishing of the flame.

By repeating similar experiments with gas-air mixtures of different compositions we can verify that a reduction in the content of air in the mixture expands the limits of stable combustion. In fact, the less air in the composition of the mixture the less gas is burned in the cone of the primary flame and, consequently, the deeper will be the diffusion flame. This flame is actually the combustion stabilizer, ensuring continuous ignition of the gas-air mixture at the extreme periphery of the base of the primary flame cone. Consequently, the less air in the mixture the higher the mixture outlet velocity which is required to cause flame separation. On the other hand, in Chapter III we saw that the normal velocity of propagation of a gas-air mixture depends on its composition and is reduced with a reduction in the air content. Consequently, the outlet velocity of the mixture at which penetration of flame into the tube occurs should also be reduced.

Analogously we can verify that an increase in the air content in the mixture narrows the limits of stable combustion. The reasoning which leads to this conclusion remains virtually the same. With an increase in the air content in the mixture the center of gravity of combustion is transferred to the primary flame cone; diffusion combustion is weakened and its ability to stabilize the primary combustion is reduced. Therefore the outlet velocity of the mixture at which flame breakaway occurs is also reduced. Along with this the flame propagation rate is increased and along with it the outlet velocity of the mixture at which penetration of the flame into the tube occurs is also increased.

All of the above is illustrated graphically by the curves depicted on Fig. 49. The content of air in the mixture is plotted on the horizontal axis, while the outlet velocity of the mixture

is plotted on the vertical; in this way we can construct the two limiting curves of stable combustion: lower curve 1, which shows at what outlet velocity penetration of flame into the tube is observed for different gas-air mixtures, and upper curve 2, showing the outlet velocity at which flame breakaway is observed for different gas-air mixtures. The fact that the shape of the lower curve completely repeats the shape of the curves of the change in velocity of flame propagation as a function of mixture composition (see Fig. 30) is immediately noticeable. This is in complete agreement with our reasoning, since it shows a direct dependence of penetration velocity on the velocity of flame propagation. More than this, this curve ends precisely on the lower (right) and upper (left) limits of flammability of the mixture. This means that beyond these limits the phenomenon of flame penetration [into the tube] cannot be observed, since in such mixtures no flame is propagated at all.

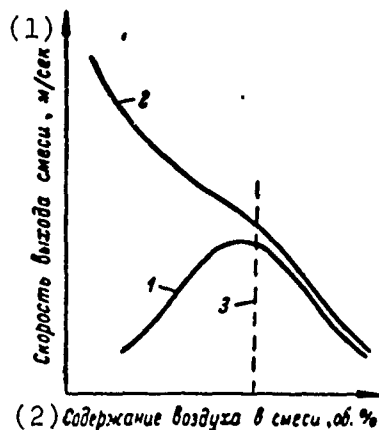


Fig. 49. Curves of flame stability during combustion of a gas-air mixture.

KEY: (1) Mixture outlet velocity, m/s; (2) Air content in mixture, vol. %.

With an increase in the content of air in the mixture the upper curve drops steeply downward from the very high values of flame breakaway velocity characteristic for pure gas (i.e., a mixture with a zero oxygen content) for mixtures very rich in gas and, after [crossing] vertical line 3, corresponding to a stoichiometric composition, approaches so closely the lower curve that combustion for such a mixture is unstable for practical purposes.

This position holds true also for mixtures containing an excess quantity of air.

On the right side the upper curve terminates, like the lower curve, on the lower ignition limit. This attests to the fact that combustion of a jet of gas-air mixture containing an extreme excess of air and falling outside the ignition limits is, in general, impossible.

Combustion of a Turbulent Gas-Air Jet

As was already pointed out, during combustion of a gas-air jet a laminar flame will continue to be stable and is usually broken away from the burner prior to the appearance of turbulence, but if continuous ignition of the jet at its base is ensured it is possible to obtain also a stable turbulent flame. Naturally, such a flame differs from a laminar flame in both external appearance and internal structure. It will no longer have a thin and sharply outlined azure cone. Primary combustion is, as it were, scattered in space (this is especially noticeable in the central portion of the jet) and has not clear outlines, but blurred and pulsating configurations.

In order to analyze the structure of the flame under various developments of turbulence it is necessary to use the concept of the turbulence scale; here we understand the linear dimension of the elementary volume of gas in which in a given time span all particles possess identical velocities of motion. This quantity can also be interpreted as the average diameter of eddies or as the path which an elementary volume of the gas travels in the period of its existence - i.e., from the moment of formation to the moment of decay.

The concept of a scale of turbulence permits us to divide turbulent flows into two types, different in principle - flows

with small-scale turbulence, characterized by a small turbulence scale and large velocity pulsations, and flows with large-scale turbulence; these are characterized by a large turbulence scale and small velocity pulsations.

The structure of a turbulent flame during combustion of a gas-air mixture differs as a function of the turbulence scale; however, in all cases it differs from the structure of a laminar flame, since the latter (as was already indicated) represents a thin layer of reacting mixture with a smooth surface (Fig. 50a). During small-scale turbulence, when the scale of turbulence is small as compared with the thickness of the reacting layer, the latter retains its continuity in space but its surface becomes more uneven and wavy. As a result of this the visible thickness of the flame, δ_T' , grows and becomes greater than the thickness of the laminar flame, δ_n (Fig. 50b). Naturally, the increase in the surface of the combustion front which is connected with this corresponds to an ever more intense nature of combustion. With transition to conditions of large-scale turbulence the waviness of the surface of the combustion front becomes so substantial that individual small volumes of burning mixture begin to be broken away from it; these are further broken up by subsequent pulsations and are burned out. Then the entire front is broken up and transformed into a system of individual foci of combustion, filling a layer with thickness δ_T'' (Fig. 50c). In this case combustion of the mixture is intensified even more.

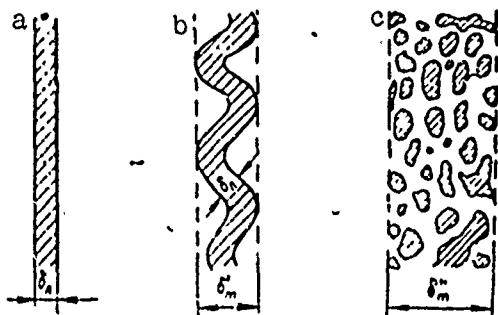


Fig. 50. Structure of combustion zones under various conditions of gas-jet motion.

The mechanism of turbulent combustion of a gas-air mixture can be presented in various ways. According to the presentations called the "frontal" theory of turbulent combustion, small individual volumes of mixture which occupy the volume of the visible turbulent flame burn from the surface, where combustion penetrates into their depth at a rate equal to the normal velocity of flame propagation. The sharp growth in combustion intensity as compared with a laminar flame is connected with the increase in the total combustion surface. These ideas are countered by the theory of "volume" combustion, according to which the individual volumes of gas-air mixture burned not from the surface, but in the volume itself, with the latter being heated by the penetration of surrounding hot combustion products.

It should be noted that both the above theories were put forward only for purposes of mathematical analysis of the process of turbulent combustion of a gas-air mixture, an extremely complex process, in order to simplify it and provide a rough picture. There is no question that in actuality both frontal and volume combustion occurs simultaneously in a turbulent flame of this type, and if it were possible to "freeze" the processes occurring in it at some instant and then to study the combustion zone it would be possible to find within its limits both finite volumes of pure gas-air mixture, bounded by a flame front directed inward, and finite volumes of mixture so diluted by hot combustion products that ignition occurs throughout their entire volume.

At the same time, naturally, for experimental determination of the rate of turbulent propagation of the flame one should proceed either from the first or the second theory. In fact, if we assume that the visible smearing of the combustion zone is explained by pulsations of a thin twisted flame front around a certain average position, the average rate of flame propagation should be calculated by dividing the flow rate of the mixture by the magnitude

of the surface which passes somewhere between the extreme visible outlines of the flame - its upper and lower boundaries.

This approach assumes spatial continuity of the pulsating ignition surface; considering the substantial distance between the lower and upper boundaries of pulsations this seems to have a low probability. Therefore it can be contrasted to the scheme of volume combustion by representing the flame at any given moment as the totality of individual elementary volumes of mixture on different stages of the process: some not yet ignited, others in the ignition and combustion stage, and a third group in which the chemical reaction has already been completed. Naturally, elements of the first type will predominate near the lower boundary of the flame; in the central portion elements of the second type will be dominant, while the third type will predominate close to the upper boundary of the flame. With such a statement of the question it is possible to take the quotient from division of the mixture flow rate by the magnitude of the lower conical surface bounding the flame as the turbulent velocity of flame propagation.

As in the case of flame propagation in an immobile gas-air medium or in a laminar flow, its velocity in a turbulent jet depends on the concentration of combustible gas in the mixture and changes according to the same law as this concentration. The corresponding curves have a characteristic bell-shaped form and are displaced more and more upward as the velocity of the jet is increased (with a consequent increase in the degree of turbulence). The value of the boundary velocity at the lower and upper concentration limits of ignition is increased correspondingly.

In conclusion we should note that the rate of propagation of a flame in a laminar flow is used as the initial magnitude in practical calculations of gas burners, despite the fact that in the overwhelming majority of cases the ignition of gas-air mixtures

occurs in conditions of well-developed turbulent flow. The difference noted above in the magnitude of the velocities of flame propagation is taken into account only by the introduction of the corresponding correcting coefficients, obtained by purely experimental means. The theory of turbulent combustion is not as yet developed to a degree sufficient for obtaining reliable initial data for practical calculations.

Burnout Curves of a Gas-Air Flame

When photographs of an azure cone are examined a small aureole around the outside edge of the bright reaction zone is clearly visible. This indicates that even when $\alpha \geq 1$ the combustion in a laminar flame is not totally complete within the limits of an extremely narrow zone of reaction, as was assumed above, and is completed only at a certain distance from the ignition front. An experimental study carried out with a stoichiometric mixture of carbon monoxide with air confirms this result of visual observation. Figure 51 shows curves obtained for the dependence of CO_2 content in combustion products on the distance to the peak of the azure cone - i.e., to the ignition front. All the curves approach the horizontal line $\text{CO}_2 = 34.7\%$ asymptotically; this corresponds to the composition of products from complete combustion. The nature of these curves indicates that combustion is extended over a length on the order of 40-50 mm; while at normal pressure about 80% of the initial gas is burned at a distance of 0.5 mm from the ignition front, with a reduction in pressure the fraction of gas burned on this segment is noticeably reduced.

As would be expected, the temperature curves obtained in this same study indicate a correspondence between flame temperature and CO_2 yield. The temperature grows with increasing distance from the ignition front, reaching a maximum at a certain distance and then beginning to drop due to the mixing of combustion products with the surrounding air.

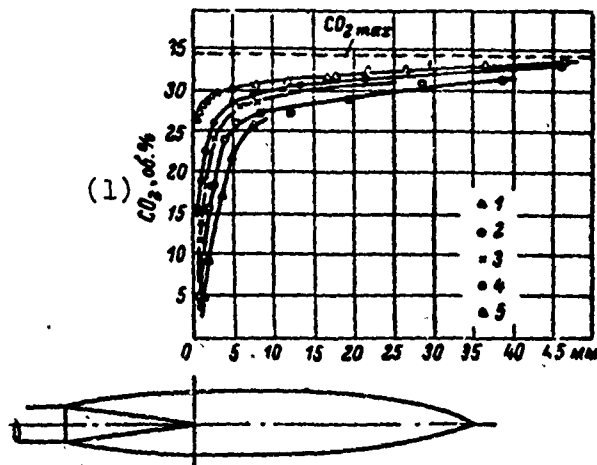


Fig. 51. Burnout curves for a gas-air mixture in a laminar flame.
 Pressure, mm Hg: 1 - 760; 2 - 402;
 3 - 300; 4 - 244 (reheat 260°C);
 5 - 182 (reheat 370°C).

KEY: (1) CO₂, vol. %.

The picture of burnout of combustible components of a mixture in a turbulent flame is completely different than that in a laminar flame. Where the latter is characterized by the fact that at each point the concentration of combustion products is constant in time and its dependence on the distance of the given point to the ignition front is depicted by a continuous line rising steeply from zero to 80% inside a zone 0.5 mm thick (as shown on Fig. 51) and then continuing to rise, not so steeply but smoothly, within the limits of the precombustion zone, this does not occur in a turbulent flame. It was already pointed out that the combustion zone in a turbulent flame represents, as it were, a finely-broken mosaic comprised of individual flow elements in different stages of the combustion process and also continuously changing their position in space. In accordance with this the content of combustion products at all points of the combustion zone is a quantity which varies in time, while the burnout factor, representing the fraction of already combusted gas, can vary within the limits 0 to 100%.

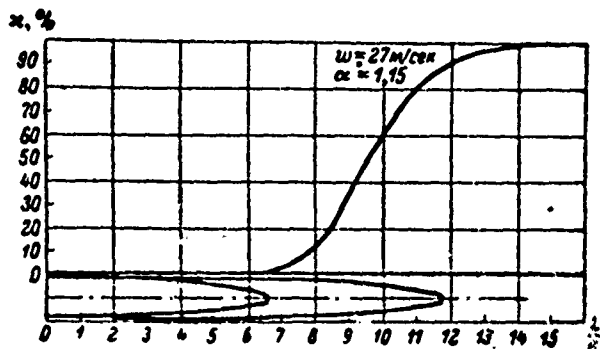


Fig. 52. Burnout curves for a gas-air mixture in a turbulent flame.

Designation: м/сек = m/s.

Along with this, it is natural that values of the burnout coefficient averaged in time at each point should be constant and depend on the relative distance to the burner edge. This is confirmed by experiments carried out with a mixture of Moscow city gas with air at $\alpha = 1.15$; the results of these studies are presented on Fig. 52. As is evident from the graph, burnout of the mixture in the flame occurs gradually, since the curve of the change in the burnout coefficient κ from 0-3% on the inner boundary of the flame gradually grows to 80-90% on the outer boundary. The final segment of this curve, where the burnout factor reaches 100%, lies outside the visible zone of combustion. Here, as in the case of a laminar flame, residues of combustible gas undergo afterburning; however, since the intensity of this process is quite small the characteristic luminescence is absent — the factor which represents a principle difference between the zone of afterburning and the combustion zone ahead of it.

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